MICROMIXING EXPERIMENTS

In the Introductory Chemical Reaction Engineering Course

KEVIN D. DAHM, ROBERT P. HESKETH, MARIANO J. SAVELSKI
Rowan University • Glassboro, NJ 08028-1701

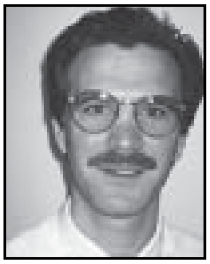
In practice, the issue of mixing and chemical reactions is very important in the economic aspects of chemical reaction engineering. A major priority in industrial reactors[1] is to optimize the yield of desired products. This optimization is a function of reactor geometry, the chemical and physical characteristics of the reacting system, the degree of mixing, and the mode of supplying the reactor with reagents. Bourne and Gablinger[2] have shown how process chemistry developed in the laboratory can go awry when scaled to industrial reactors. An excellent example of the classic series-parallel reaction using an azo dye chemistry is presented by Bourne and Gholap.[3] A chemist working on a bench scale will optimize this reaction to obtain very high reaction rates for the desired reaction. In the industrial scale reactor, micromixing becomes a limiting factor, negatively impacting the process chemistry.[4]

As Etchells[5] noted, however, a typical undergraduate reactor design course focuses on ideal reactors. In the chapter on multiple reactions in the standard chemical reaction engineering text by Fogler,[6] it is assumed that the reactions are slow compared to the mixing of species. The classic examples for parallel reactions and series reactions are given, but these examples do not cover the basic concept of micromixing with respect to the reactants. It is only in the final chapter of this text that the concept of micromixing is introduced, and the presented mathematical theory is relatively complex for undergraduates.

Idealized reactor models provide an excellent framework for a conceptual introduction to reaction engineering and reactor design, but they can be easily misused. In attempting to use ideal reactor models for the azo dye system, for example, one would overlook the impact of mixing on the reaction kinetics and on the formation of trace byproducts. A thorough treatment of the modeling of micromixing is beyond the scope of the introductory undergraduate chemical reaction engineering course, but the experiments described in this paper provide a qualitative and quantitative demonstration of the significance of the mixing effect and the limitations of the idealized reactor models, with minimal time investment.

Baldyga and Bourne[7] summarize a number of experimental examples of product distributions sensitive to mixing. Examples of parallel or competitive reactions include Diazo

***Kevin D. Dahm** is Associate Professor of Chemical Engineering at Rowan University. He received his PhD in 1998 from Massachusetts Institute of Technology and his BS in 1992 from Worcester Polytechnic Institute. Prior to joining the faculty of Rowan University, he served as an Adjunct Professor of Chemical Engineering at North Carolina A&T State University and a postdoctoral researcher at the University of California at Berkeley.*



***Robert P. Hesketh** is Professor of Chemical Engineering at Rowan University. He received his BS in 1982 from the University of Illinois and his PhD from the University of Delaware in 1987. After his PhD, he conducted research at the University of Cambridge, England. Robert's teaching and research interests are in reaction engineering, green engineering, and separations.*

***Mariano J. Savelski** is Associate Professor of Chemical Engineering at Rowan University. He received his BS in 1991 from the University of Buenos Aires, his ME in 1994 from the University of Tulsa, and his PhD in 1999 from the University of Oklahoma. His technical research is in the area of process design and optimization. His prior academic experience includes two years as Assistant Professor in the Mathematics Department at the University of Buenos Aires, Argentina.*

coupling with simultaneous reagent decomposition[8] and Iodate/iodine reaction with neutralization.[9] Examples of parallel-series reactions or competitive-consecutive reactions include Diamines with isocyantes or other acylating agents, nitrations of dibenzyl, durene, and alkyl benzenes and diazo couplings. The experiments described in this paper involve this pair of parallel competitive reactions, carried out in an aqueous solution:

$$H_2BO_3^- + H^+ \leftrightarrow H_3BO_3 \qquad (1)$$

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (2)$$

The first reaction is essentially instantaneous, and can be modeled as an equilibrium reaction with $K = 1.38 \times 10^6$ at ambient conditions.[10,11] The second reaction is essentially irreversible, with a rate that is first order in concentration of IO_3^-, second order in I^- and second order in H^+. The rate constant has been modeled as a function of the ionic strength of the solution[9,10] and at the conditions of this reaction, $k_2 \sim 3.6 \times 10^7\ M^{-4}sec^{-1}$. Thus the second reaction is fast, but orders of magnitude slower than the first reaction. So when H^+ is added as the limiting reagent, a perfectly mixed system would produce essentially no I_2. Production of a significant quantity of I_2 is attributed to a local excess of H^+; a condition in which all $H_2BO_3^-$ in a region is consumed and H^+ remains to react with I^- and IO_3^-.

Figure 1.

2-L reactor with Lightnin mixer.

Reagent	Concentration (mol/l)	MW (g/mol)
H_3BO_3	0.606	61.83
NaOH	1.0	40.0
KIO_3	0.0233	214
KI	1.167	166
H_2SO_4	0.50	98.04

Any I_2 formed in solution will react further with I^-

$$I_2 + I^- \leftrightarrow I_3^- \qquad (3)$$

The concentration of the I_3^- ion can be measured accurately with spectrophotometry and Beer's law. Thus, the yield of reaction 2 is readily determined. Consequently, this reaction was deemed suitable for an undergraduate experiment because it meets several important criteria:

- *The reagents are readily available, cheap, and reasonably safe, with water acting as the solvent.*
- *Quantitative results can be obtained with a fairly simple analytical method.*
- *The kinetics of both reactions have been studied.[9-11]*
- *Imperfect mixing has an effect on product distribution that is straightforward to quantify and explain.*
- *Finally, the iodine formed in solution has a striking yellow color. This is a perk compared to a solution that remains transparent throughout the reaction because the solution* ***appears to be homogeneous.*** *The yellow color grows darker as the reaction progresses but appears uniform at any given time. The fact that something can be well mixed macroscopically but poorly mixed on a molecular level is an important take-home message of this experiment.*

The experiment was integrated into a junior course on chemical reaction engineering in the Spring 2003 semester. The remainder of this paper describes the experimental apparatus itself, provides sample results, discusses the integration of the experiment into the course, and gives the results of a short quiz that was administered to assess the impact of the experiment.

APPARATUS

A team of Rowan undergraduate students designed and assembled the apparatus and developed an experimental procedure as an Engineering Clinic[12] project. There are two distinct experimental setups: one uses a 2-L reactor with baffles and a Lightnin Mixer (shown in Figure 1) and the other uses an ordinary 600-mL beaker with a magnetic stirring bar. In the first setup, a syringe pump is used to add the limiting reagent, sulfuric acid, at a controlled, known rate. In the second setup an Eppendorf pipet is used to add the acid all at once. Both experiments require stock solutions as summarized in Table 1. The purpose of the sodium hydroxide is to neutralize a portion of the boric acid, so that the $H_2BO_3^-$ ion will be present with a concentration of 0.02 mol/L when the addition of sulfuric acid begins.

EXPERIMENTAL PROCEDURE

The impeller speed of the mixer is the parameter that was varied, spanning the range outlined in Figure 3. The experimental procedure developed for the Lightnin Mixer is as follows:

1) Fill reactor with the 1080ml of DI water.
2) Add 225ml of the H_3BO_3 solution.
3) Add 30ml of the NaOH solution.
4) Add 150ml of the KIO_3 solution.
5) Start mixer at 500 rpm (regardless of desired experimental speed) and allow solution to mix thoroughly.
6) Add 15ml of the KI solution. Let solution mix for several minutes to insure homogeneity.
7) Reset mixer to experimental speed.
8) Inject 10 ml of the sulfuric acid solution with the syringe pump, at a rate of 50 mL/hr.
9) After injection is complete, wait approximately 2 minutes (to insure homogeneity of the solution) then turn off mixer.
10) Take samples from various points in the reactor.

Because the first reaction is essentially instantaneous and the second essentially irreversible,{9,10} the composition does not change in the two minutes after the addition of acid is completed, but the mixing in step 9 ensures that the samples taken will be representative of the solution as a whole.

The procedure for the beaker-stirring bar system is analogous. The total solution volume 300 mL rather than 1.5 L as in the Lightnin Mixer but the proportions of the reagents used are the same. The analysis of samples was completed using a Spec220, with the following procedure:

1) Set the wavelength to 353nm, the sensitivity to high, and the mode to Absorbance.
2) Fill one quartz cuvet with DI water and set the absorbance of this control sample to zero.
3) Take 1 mL of sample using Eppendorf pipet and inject into 10-mL volumetric flask. Fill the remainder of the 10-mL volume with DI water (mix well).
4) Pour the diluted sample into a quartz cuvet. Take to Spec220 and read the absorbance (reading should be between 0 and 1.999; if not, change the dilution as needed.)

DATA ANALYSIS

A calibration curve relating I_3^- concentration to absorbance is shown in Figure 2. The I_3^- concentration is quantified by applying Beer's law

$$C_{I_3^-} = \frac{A}{\varepsilon \ell} \qquad (4)$$

The I_2 and I^- concentrations can then be deduced from the following known equilibrium relationship for reaction (3):[13]

$$\text{Log}\left(K_{eq}\right) = 555 / T(K) + 7.355 - 2.575 \cdot \text{Log}[T(K)] \qquad (5)$$

Thus, one can deduce the extent of reaction 2, and by applying standard chemical reaction engineering principles of species balances and

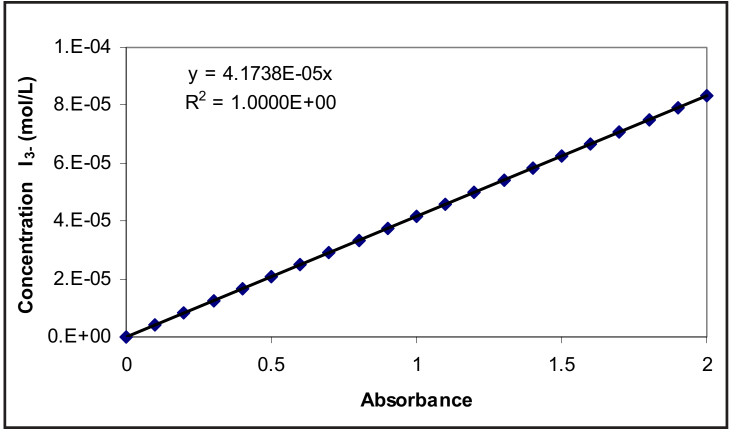


Figure 2. *Calibration curve for I_3^- ion concentration.*

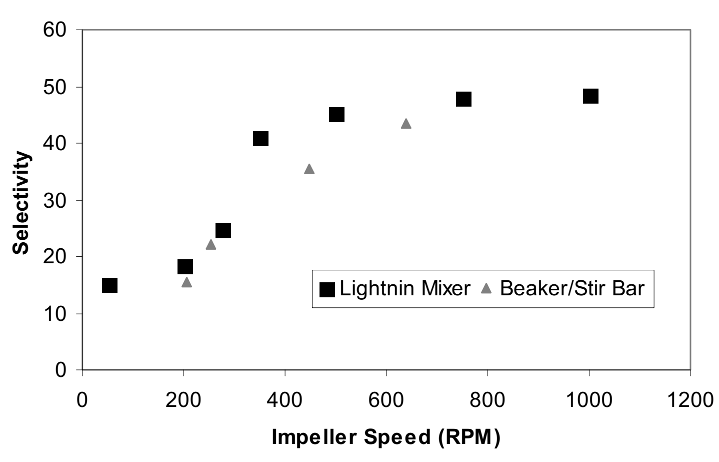


Figure 3. *Effect of increased mixing on selectivity of reaction 1 to reaction 2.*

equilibrium relationships, one can compute the amounts of the added H^+ that were consumed by reactions 1 and 2, respectively. These fractions are a function of the rate of micro-mixing.

The product distribution can be quantified using the same method as Guichardon and Falk,[10] in which two limiting conditions are identified:

> ***Perfect Mixing*** in which the system acts like the perfectly mixed CSTR familiar to the students from early in the reaction engineering course. In this system, the yield of reaction 2 is insignificant under perfect mixing.
>
> *Total Segregation* describes a system in which micro mixing is infinitely slow, so both reaction rates are essentially instantaneous by comparison. In this situation the rates of reaction 1 and 2 will be in proportion with the local concentrations of $H_2BO_3^-$ and I^-, and independent of the kinetic rate constants of the reactions.

Guichardon and Falk characterize the system by dividing the total volume of the reactor into a "perfectly mixed volume" V_{PM} and a "totally segregated volume" V_{TS}. The "micromixedness ratio," α, is defined as V_{PM}/V_{TS}. Details of calculating α for this system are given in their paper.[10] The calculation of α, however, was deemed beyond the scope of the one-period introduction to micromixing presented in this paper. Instead, the more familiar selectivity was used to quantify the results, and the total segregation and perfect mixing models were presented qualitatively as an explanation for the disparity between observed and predicted selectivity.

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Selectivity throughout this paper is defined as:

$$S = \frac{\text{moles } H^+ \text{consumed by reaction 1}}{\text{moles } H^+ \text{ consumed by reaction 2}} \qquad (6)$$

Figure 3 shows the selectivity vs. impeller speed for both experimental setups. Note that in both cases an increase in impeller speed leads to an increase in selectivity. This observation helps demonstrate to the students that poor mixing is indeed the reason for the discrepancy between prediction and observation.

The two experiments were carried out with different volumes to demonstrate the relationship between scale and mixing, which was cited in the introduction to this paper as a major motivation for teaching micromixing. The larger-scale experiment used a better impeller, a vessel with baffled walls, and a slow, controlled rate of addition of the limiting reagent, all factors that are known to produce better mixing. Quantitative modeling of the effects of these differences is possible with, for example, the E model of inhomogeneous turbulence.[6] While such a theoretical treatment is again beyond the scope of this module, students readily agree that qualitatively, the larger reactor is better designed to achieve good mixing. The data show, however, that the selectivity curves are in fact very similar for the two experimental setups, because the increase in scale offsets the benefits gained from using better equipment.

CLASSROOM USE OF MICROMIXING EXPERIMENT

The Spring 2002 offering of chemical reaction engineering included one 75-minute class period devoted to micromixing. The topics discussed in this period were:

- *Why mixing rates and reaction rates can be interrelated*
- *Qualitative coverage of the concepts of perfect mixing and total segregation*
- *The "perfectly mixed" and "totally segregated" reactor models.*

At the conclusion of this period, the instructor explained that real reactors could be modeled as a combination of a "perfectly mixed" volume and a "totally segregated" volume. The purpose of this class period was to illustrate the shortcomings of the idealized reactor models that had been used throughout the semester. The presentation was in a lecture format and used sample data produced with POLYMATH,[14] but had no experimental component.

During the Spring 2003 semester, the course included a 100-minute period devoted to micromixing. The topical coverage was the same as in the 2002 session, but this time, the experiment was integrated. Students were first shown the pair of competetive reactions and the initial composition of the reactor (excluding the H_2SO_4). The rate expression for reaction 2, as discussed in the introduction section, is

$$r_2 = k_2[H+]^2[I^-]^2[IO_3^-] \qquad (7)$$

The rate expression for reaction 1 was presented as

$$r_1 = k_1\left([H+][H_2BO_3^-] - [H_3BO_3]/K_1\right) \qquad (8)$$

with $K_1 = 1.38 \times 10^6$ and $k_1 = 10^{17}$. (The value of k_1 is not important so long as it is set sufficiently high that the reaction is in effect modeled as an instantaneous equilibrium reaction.)

A common teaching technique used throughout this course was for the instructor to pose a problem and then challenge the students to derive model equations describing the system. Once this was completed, the instructor would distrubute handouts showing a POLYMATH solution of the equations. In this case, the applicable design equation from Folger's text[6] is the semibatch equation

$$\frac{dC_B}{dt} = r_B + \frac{\nu_0 \left(C_{BO} - C_B\right)}{V} \tag{9}$$

in which the addition term is 0 for all species except the acid, which is added gradually as the limiting reagent. When simultaneous species balances for the reaction system described here were solved, the selectivity was 3800.

The students next proceeded to the laboratory, where the setup (steps 1-7) for an experiment with the Lightnin mixer had already been completed. Students recognized this as a semibatch reactor—a mixed vessel with all reactants initially present except for one that was slowly added. When the addition of acid was started, the solution immediately turned yellow—qualitative evidence that iodine was present in significant quantities. The experiment and sample analysis was completed as a demonstration. The demonstration ended with the calculation of the overall selectivity, which was on the order of 10^1.

The instructor then presented the data shown in Figure 3, saying "the experiment we just did would be one point on this graph." The data show that the baffled reactor with the Lightnin mixer provides a slightly higher selectivity (despite the larger scale) than an unbaffled beaker with a stir bar, and in both setups the selectivity of reaction 1 increases as the impeller speed increases. Both observations are evidence that mixing influences the reaction kinetics.

The instructor then continued with a discussion of micromixing and the "perfectly mixed" and "totally segregated" models that had also been presented in the Spring of 2002. This model allows quantitative prediction of selectivities,[7] but the calculations were beyond the intended scope of this one-period introduction. Consequently, the ideas of perfect mixing and total segregation were presented as qualitative explanations of why mixing influences the kinetics of fast reactions.

It is important to note that in both 2002 and 2003, the topical coverage of the introduction to micromixing was the same, and in both years students were responsible for the material and there was a 10-point question on micromixing on the final exam. The only difference in the presentations was the use of an experimental demonstration in the second year. The rest of the course was also substantially the same in both years and used the same syllabus and Fogler's book as the text.

In the spring of 2004, micromixing was not covered at all in the chemical reaction engineering course. In this offering of the course (and in the previous two years), students were responsible for the derivation of the CSTR design equation on the first exam, so students were exposed to the asssumptions, including perfect mixing, behind the equation. In order to provide a contrast with previous years, however, micromixing was not covered through lecture or lab.

ASSESSMENT OF EXPERIMENT

The anecdotal feedback on the micromixing experiment was favorable. Students appreciated seeing the real equipment and expressed surprise that a system that qualitatively looked well-mixed behaved so differently from an ideal reactor. The primary goal, however, was to prevent future misuse of the idealized reactor models by illustrating their shortcomings. In an attempt to assess the effectiveness of this, in September of 2002, 2003, and 2004, the following question was included in a non-graded "assessment quiz" that was administered to the senior classes.

> *Our specialty chemical pilot plant includes a reactor that is a ~20-L kettle with a steam-heating jacket and an agitator. You are asked to model the reactor and a classmate has suggested using the CSTR design equation that you learned in chemical reaction engineering last spring. Is this appropriate? If your answer is "yes" or "no," explain why, and if it is "maybe," explain what factors it depends upon.*

There were three other questions on the quiz, covering Bernoulli's equation, vapor pressures and dew points. The students were told that the quiz was intended to assess retention of concepts from the junior year, but were not told there was a specific agenda of assessing the micromixing experiment. For each class this quiz was unannounced, was closed-book with no preparation of any kind, and was adminstered five months after the conclusion of the chemical reaction engineering course.

TABLE 2
Student Responses to Whether or Not It is Appropriate to Use CSTR Design Equation for 20-L Agitated Reactor

Date	*"Yes"*	*"No"*	*"Maybe"*
September 2002	4	0	17
September 2003	1	0	14
September 2004	4	1	11

TABLE 3
Factors Cited by Students Who Responded "Maybe"

Date	*Steady-State or Not*	*Mixing*
September 2002	13	4
September 2003	12	5
September 2004	7	0

> ***While a thorough coverage of mixing and chemical kinetics is beyond the scope of most introductory chemical reaction engineering courses, this experiment introduces students to the field and illustrates the limitations of the idealized reactor models.***

The student responses to this question are summarized in Tables 2 and 3. All three years, most students said "maybe," with some mention of whether the process was "continuous" or "steady-state," (as opposed to "batch or semi-batch") being most commonly cited as the determining criteria. The fraction of students, however, who specifically mentioned "perfect mixing" in their response increased from 19% (4 of 21) to 33% (5 of 15) in the second year, and was zero for the 2004 control group, who were not exposed to micromixing. The students who answered "yes," in all cases used the rationale that because the reactor has an agitator, it must be a CSTR—exactly the sort of error that this introduction to micromixing was intended to prevent. The number of students who responded this way dropped from 19% (4 of 21) to 7% (1 of 15) the second year, and was 23% (4 of 17) in the control group.

A Chi-squared analysis of the differences between the three classes cited in the last paragraph was performed. This showed:

- *The second class (lecture and lab) performed better on the quiz than the first (lecture only) class but the improvement was not statistically significant at 95% confidence (p~0.3).*
- *The first class (lecture only) performed better than the control group. This difference was also not statistically significant at 95% confidence (p~0.1).*
- *The differences between the second class (lecture and lab) and the control group was statistically significant to (p~0.02).*

Thus, the quiz indicates that an introduction to micromixing achieved the goals of improving retention and illustrating the limitations of the idealized reactor models, but no statistical conclusion can be drawn regarding whether the improvement was primarily attributable to the lecture, the lab, or both.

SUMMARY AND CONCLUSIONS

The traditional chemical reaction engineering course is taught using idealized reactor models, such as the CSTR and the PFR models, with little discussion of mixing. This paper presents a micromixing experiment and its use in an introductory chemical reaction engineering course. While a thorough coverage of mixing and chemical kinetics is beyond the scope of most introductory chemical reaction engineering courses, this experiment introduces students to the field and illustrates the limitations of the idealized reactor models.

A quiz was administered to the students five months after the course was completed. The results suggested that an introduction to micromixing using this experiment is helpful for illustration and retention of the concepts.

ACKNOWLEDGEMENTS

Support for the laboratory development activity described in this paper was provided for by a grant (DUE- 0088501) from the National Science Foundation through the Division for Undergraduate Education. The authors gratefully acknowledge the following undergraduate students who contributed to this project: Robert McKeown, Andrew Dunay, David Urban, Danielle Baldwin, William Engisch, and Shaun Rendall.

REFERENCES

1. Belkhiria, S., T.Meyer, A.Renken, "Study of Micromixing in Polymerization Reactions and Its Application in Experimental Copolymerization," in *Industrial Mixing Technology: Chemical and Biological Applications*, E.L.Gaden, Jr., G.B.Tatterson, R.V.Calabrese, W.R.Penney, eds., AIChE Symp. Ser., Vol. 90, No. 299 (1994)
2. Bourne, J.R., H. Gablinger, "Local pH Gradients and the Selectivity of Fast Reactions. II. Comparisons Between Model and Experiments," *Chem. Eng. Sci.,* **44**(6), 1347 (1989)
3. Bourne, J.R., R.V. Gholap, "Approximate Method for Predicting the Product Distribution of Fast Reactions in Stirred-Tank Reactors," *Chem. Eng. J. and Biochem. Eng. J.,* **59**(3), 293 (1995)
4. Baldyga, J., J.R. Bourne, S.J. Hearn, "Interaction Between Chemical Reactions and Mixing on Various Scales," *Chem. Eng. Sci.,* **52**(4), 457 (1997)
5. Etchells, A., "Notes on Mixing in the Process Industries: Lecture and Short Course Material," DuPont USA, Wilmington, DE (1998)
6. Fogler, H. Scott, *Elements of Chemical Reaction Engineering,* 3rd ed., Prentice Hall PTR, New Jersey (1999)
7. Baldyga, J., and J.R. Bourne, *Turbulent Mixing and Chemical Reactions*, John Wiley & Sons, Chichester (1999)
8. Nienow A.W., S.M. Drain, A.P. Boyes, R. Mann, A.M. El-Hamouz, and K.J. Carpenter, "A New Pair of Reactions to Characterise Imperfect Macromixing and Partial Segregation in a Stirred Semi-Batch Reactor," *Chem. Eng. Sci.,* **47,** 2825 (1992)
9. Fournier, M.C., L. Falk, and J. Villermaux, "A New Parallel Competing Reaction System for Assessing Micromixing Efficiency: Experimental Approach," *Chem. Eng. Sci*., **51**, 5053 (1996)
10. Guichardon, P., and L. Falk, "Characterization of Micromixing Efficiency by the Iodide-Iodate Reaction System. Part I: Experimental Procedure," *Chem. Eng. Sci.,* **55**, 4233 (2000)
11. Guichardon, P., L. Falk, and J. Villermaux, "Characterization of Micromixing Efficiency by the Iodide-Iodate Reaction System. Part II: Kinetic Study," *Chem. Eng. Sci.,* **55**, 4245 (2000)
12. Schmalzel, J., A. Marchese, and R. Hesketh, "What's Brewing in the Engineering Clinic?" *Hewlett Packard Engineering Educator*. **2(1)**, 6 (1998)
13. Palmer, D.A., R.W. Ramette, and R.E. Mesmer, "Triodide Ion Formation Equilibrium and Activity Coefficients in Aqueous Solution," *J. Solution Chem.*, **13**, 9, (1984)
14. Shacham, M., N. Brauner, and M.B. Cutlip, "Efficiently Solve Complex Calculations," *Chem. Eng. Prog.,* **99,** 10 (2003) ❐