

DISMT – Determination of Mixing Time through Color Changes

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ABSTRACT

The DISMT (“Dual Indicator System for Mixing Time”) mixing time/distance diagnostic encodes semi-quantitative visualization of liquid/liquid mixing processes in color changes. In DISMT, two liquids, one red and one blue, are mixed to produce a yellow liquid. Through appropriate choice of the acid-base indicators used, and the initial pH’s of the two solutions, the yellow liquid appears only in those regions where the mixing fraction is within a designated fractional deviation (say 5%) of the infinite time mixing fraction. Thus, the 95% mixing time/distance can be defined, for the whole volume of the mixing system, as the time/distance for all of the liquid to become yellow.

This paper describes: (1) the principles underlying and choices involved in the design of DISMT systems, (2) protocols for carrying out DISMT-based experiments, and (3) examples of results obtained with DISMT.

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I. Introduction

There are several classes or types of industrial mixing problems in which the approach to the final homogeneous state is critical to the design engineer. The problems can be as commonplace as the tank mix blend time for homogeneous blending operation or as specific as the design of a continuous reactor in which a static or dynamic mixer is required in order to minimize formation of undesired byproduct. Frequently, a characteristic mixing time has been used to provide an (oversimplified) summary of the mixing process. However, in those cases in which the development of the design permits the use of an optically accessible mixing system, a much more informative variety of fluid flow and mixing diagnostics may be applied. This paper describes one such diagnostic.

Mixing is fundamentally the evolution in time of spatially dependent concentrations toward a final homogeneous state. In an ideal world, researchers studying mixing processes would have access to concentration maps of the relevant species in the entire vessel as a function of time. In the current world, researchers have to deal with less than ideal data. Chemical sampling is intrusive and provides point-wise data at very low sampling rates. Colorimetric probes are intrusive and provide point-wise data as a continuous function of time. Planar laser induced fluorescence measurements are non-intrusive and provide 2-D concentration images, at typical sampling rates of only a few hertz. Other useful techniques fall within these bounds. All fall considerably short of the goal of quantitative concentrations measured non-intrusively for the whole volume of the vessel at arbitrary sampling times. The reaction-based colorimetric diagnostic method described in this report attempts to address part of these limitations; it provides semi-quantitative, but valuable, concentration information coupled with the possibility of complete interrogation of the vessel volume and arbitrarily fast time sampling.

DISMT (“Double Indicator System for Mixing Time”) reduces the range of concentration information reported to the question “Have these two liquids mixed on a molecular level within a specified fraction (say 5%) of the mixing fraction which will be attained in the whole vessel at infinite time?”, and it encodes the answer in the colors of the evolving mixture. It is hoped that the simplicity of use and the directness of the mixing information reported will stimulate experiments that provide substantial “engineering insight” into the dynamics of mixing.

DISMT makes use of two standard acid-base indicators, methyl red (red to yellow, pK ~ 5) and thymol blue (yellow to blue, pK ~ 9). Both indicators are added to both unmixed solutions. A red (acidic) solution is mixed with a blue (basic) solution, and in those regions where the mixing fraction is within 5% of the mixing fraction at infinite time, the solution is yellow. With a clear mixing vessel, an observer may see distinct red and blue regions as well as the later emergence of yellow regions. With DISMT, the 95% mixing time for the entire vessel may be defined as the time for the entire liquid volume to become yellow.

The following discussion of the role and utility of various mixing diagnostics makes substantial use of a review developed as part of a student thesis^[1]. The examples are intended to be illustrative rather than exhaustive.

DISMT is a reaction-based diagnostic, and thus color changes occur only when reactants have been mixed at the molecular level. Such reaction-based diagnostics avoid the ambiguities associated with dilution diagnostics and the phenomena generally referred to as “micromixing”^[2]. With dilution based diagnostics, in which for example, a non-reactive tracer dye is added to a mixing tank, the finite sampling volume of any detection system may include elements of liquid which are much smaller than the detection volume but which have not mixed on a molecular level. The detector will report only the overall mixing fraction and will not distinguish between dispersed and molecularly mixed fluids.

Many elegant reaction-based methods have been developed to characterize the rates of mixing. These include the use of competitive parallel reactions^[3-6], and fluorescence-based measurements of turbulent fluctuations^[7-8]. The methods work well, but because they make use of point-wise sampling, they report results which provide little insight into the dynamics of the mixing process.

Colorimetric methods include inert and reactive dye tracers^[9] and discoloration of colored species by reactions^[10]. When these methods are used in a volumetric – rather than point-wise fashion, they can provide substantial information about the dynamics of mixing. However, because the mixing information is encoded in the intensity of the transmitted light, these methods can give ambiguous results along the line of sight. The “one indicator” methods cannot give information about a range, say +/- 5% of ideal, for the mixing fractions.

Planar laser induced fluorescence methods provide excellent spatial resolution, without the ambiguities associated with viewing along the line of sight, for a selected plane within the mixing vessel. A variety of mixing studies have made use of planar laser induced fluorescence, with either simple dilution^[11-14] or with acid-base reactions^[15-22]. Most of the acid-base fluorescence studies have used fluorescein, whose fluorescence turns on for pH>4. More recently, dual emission fluorescence systems have been described in which mixing information is encoded in changes in the emission spectra rather than in intensities^[23]. A fluorescent diagnostic system in which the shift in the fluorescence of a solvatochromatic dye was used to image the mixing fraction in a decane/ethanol system has been described^[1]. These last two systems, with their emphasis on spectra rather than intensities, are analogous to the colorimetric DISMT system described in this work.

This paper describes: (1) the principles underlying and choices involved in the design of DISMT systems, (2) protocols for carrying out DISMT-based experiments, and (3) examples of results obtained with DISMT. Because the DISMT methods are cheap and do not give fully quantitative information, it is expected that they will find their most natural use in visualization for “engineering design”, i.e., in the heuristic design and testing of mixing systems.

II. Design of DISMT Systems

The fundamental idea underlying the DISMT method is that two color changes are used to mark two acid-base mixing fractions, $f_l = (1-\delta)*f_\infty$ and $f_h = (1+\delta)*f_\infty$, where f_∞ is the acid mixing fraction at infinite time. By appropriate adjustment of the initial pH's of the two liquids to be mixed, the pH's at these two mixing fractions will be the pK_a of the basic indicator and the pK_a of the acidic indicator, respectively. However, a variety of issues such as properties of appropriate pH indicators, routine use, sensitivity to mixing fraction, and interpretation of the color changes must be addressed.

A. Acid-Base Chemistry

The chemistry underlying DISMT is that of a strong acid/strong base aqueous titration in the presence of two weak acids, the pH indicators. The titration equation^[24] is (Ricci, 1952):

$$H - OH = a_s - b_s + (a\alpha)_1 + (a\alpha)_2 \quad (1)$$

where H = molar concentration of H^+ ;

OH = molar concentration of OH^- ;

a_s = molar concentration of strong acid;

b_s = molar concentration of strong base;

a_i = molar concentration of indicator i (in both acid and base forms, $i=1,2$);

α_i = fraction of indicator i in base form = $A_i/(A_i + H)$, ($i = 1,2$);

A_i = acid dissociation constant for indicator i , = $10^{-pK_{ai}}$, ($i=1,2$).

In acid solution OH results from the water equilibrium (and vice versa for basic solutions), and hence Equation 1 becomes, in fuller form,

$$H - W/H = H - W/OH = a_s - b_s + a_1 A_1 / (A_1 + H) + a_2 A_2 / (A_2 + H) \quad (2)$$

where W is the dissociation constant for water. In any element of the mixing liquids, $a_s = f*a_{s0}$ and $b_s = (1-f)*b_{s0}$, where a_{s0} is the concentration of strong acid in the initial, unmixed, acid solution, b_{s0} is the concentration of strong base in the initial, unmixed, basic solution, and f is the volumetric mixing fraction of the acid solution [= $V_a/(V_a + V_b)$]. V_a and V_b are the volumes of the acid solution and basic solution, respectively, in the element. The final equation is as given in Equation 3:

$$H - W/H = f*a_{s0} - (1-f)*b_{s0} + a_1 A_1 / (A_1 + H) + a_2 A_2 / (A_2 + H) \quad (3)$$

If $a_1 = a_2 = 0$, Equation 3 describes a strong acid/strong base titration, in which the pH changes strongly in the vicinity of $\log\sqrt{W} \cong 7.00$. Figure 1 shows the pH as a function of the mixing fraction f , as calculated on the basis of Equation 3, for three such titrations: $a_1 = a_2 = 1 \times 10^{-8}$ M, $a_1 = 5 \times 10^{-6}$ M, $a_2 = 2.5 \times 10^{-6}$ M (DISMT system used in demonstrations), and $a_1 = a_2 = 1 \times 10^{-4}$ M. The first two curves are virtually identical. The third curve differs substantially, an effect that will be discussed in Section IV.C.

Figure 1

If expanded, Equation 3 yields a quartic polynomial, and direct solution is not feasible. It must be solved by iterative methods.

B. Choice and Use of Indicators

The properties of an acid–base indicator which are most important are the colors of the acid and base forms, the pK_a at which the color changes, and the sensitivity to environmental (temperature and ionic strength) effects. The indicator should also be commercially available, be inexpensive, and have low toxicity.

1. Desired pK_a

In designing acid-base titrations for quantitative analysis, it is generally recommended that a pH change of 1-2 units is necessary to cause a color change sufficient to define a sharp end point. In the design of DISMT, the sharpest change of pH with mixing fraction f occurs near $pH = 7$, and consequently acid-base indicators with pK_a 's close to 7 will show the sharpest color change with as a function of f . However, if the pK_a 's are too close to 7, small errors due to impurities can have significant effects. The current DISMT system makes use of methyl red ($pK_a = 5.0$) and thymol blue ($pK_a = 9.2$) as a compromise between sensitivity to mixing fraction and insensitivity to impurities.

2. Colors and Concentrations

As the pH increases, methyl red turns from red [$\epsilon(\lambda_{\max} = 522 \text{ nm}) = 1.74 \times 10^4 \text{ L}/(\text{M}\cdot\text{cm})$] to yellow [$\epsilon(\lambda_{\max} = 428 \text{ nm}) = 1.58 \times 10^4 \text{ L}/(\text{M}\cdot\text{cm})$] at about $pH = 5$, and thymol blue turns from yellow [$\epsilon(\lambda_{\max} = 432 \text{ nm}) = 1.27 \times 10^4 \text{ L}/(\text{M}\cdot\text{cm})$] to blue [$\epsilon(\lambda_{\max} = 595 \text{ nm}) = 2.84 \times 10^4 \text{ L}/(\text{M}\cdot\text{cm})$] at about $pH = 9$. Both indicators are yellow in the pH range 5-9, the “mixed within tolerance” range, and thus the identification of yellow as “mixed within tolerance” does not depend on the concentrations of the indicators. When the pH is equal to the pK_a for methyl red (concentrations of the acid and base forms of the indicator are equal), the solution appears orange. When the pH is equal to the pK_a for thymol blue the solution appears green.

The DISMT method is designed so that $pH(f_l) = pK_a(\text{methyl red})$ and $pH(f_h) = pK_a(\text{thymol blue})$, where $f_l = (1-\delta)*f_\infty$ and $f_h = (1 + \delta)*f_\infty$. Figure 2 illustrates this effect; ideally, for $f < f_l$ the solution is blue, for $f_l < f < f_h$ the solution is yellow, and for $f > f_h$ the solution is red. Based on the experience gained in developing and testing the DISMT method, it seems that most observers perceive the color change as sharpest for δ about a factor of 2-3 larger than the design value of δ . Thus if one wishes an observer to perceive the zones in which the liquids are mixed within 5% of f_∞ , the DISMT calculations should be based on a δ which is a factor of 2-3 smaller than 0.05. In deciding what value of δ to use, the user must judge what qualitative/semi-quantitative information is desired. [It is quite possible that videotaping of the mixing experiment and subsequent computer-based hue sensitive analysis of the images can resolve this question of perception, but such techniques have not been pursued in this work. DISMT, as with any colorimetric method,

suffers from ambiguities along the line of sight, and the color of any particular portion of the mixture, viewed through liquid of a different color, may be distorted.]

Figure 2

The apparent color changes are sharper for higher concentrations (greater optical depth) of the indicators. Higher concentrations also result in sharper changes of pH with f , even though the indicators also act as buffers (see Section IV.C.). The concentrations described in this paper, 5×10^{-6} M and 2.5×10^{-6} M for methyl red and thymol blue, respectively, seem appropriate for a mixing tank 1 foot in diameter. Lower concentrations would be appropriate for larger tanks, and vice versa.

For the jet mixing experiments which were part of the development of the DISMT method, the basic (blue) liquid was injected into initially quiescent acid (red) liquid. This order was used because the blue liquid was perceived as more visible within the red liquid, rather than vice versa.

3. Sensitivity to Environmental Effects

For methyl red, $pK_a = 5.00 - 0.006*(t-20)$, for $\mu < 0.5$, where t is the temperature in degrees centigrade and μ is the ionic strength. For thymol blue, the pK_a is independent of temperature for $t = 15-30$ C, but depends significantly on the ionic strength (9.20, 9.01, 8.95, and 8.90, for $\mu = 0, 0.01, 0.05, \text{ and } 0.10$, respectively)^[25] (Bishop, 1972). In addition the pK_a for water is temperature dependent^[26] (Lide, 1982).

4. Other

Both methyl red and thymol blue are commercially available from a variety of sources. Users should consult the MSDS documents prior to use.

III. Experimental

A. Reagents and Chemical Apparatus

Methyl red, thymol blue and phenolphthalein were purchased from Aldrich. Approximately 0.100 N HCl and KOH were used to adjust the pH. De-ionized water was used in all procedures. The pH meter and electrode (Orion 230A/9107 ATC triode) were calibrated at 25 C with standard buffer solutions (pH = 7.00 and 10.00) purchased from Fisher. Ethanol was purchased from Fisher. All reagents were used as received.

Stock solutions of the indicators were prepared as follows: 202 mg of methyl red was dissolved in 200 mL ethanol (denatured) and filtered to remove undissolved particles. 10 mL of this solution in 7.5 L de-ionized water provided a concentration of $5E-6$ M. 183 mg of thymol blue was dissolved in 200 mL ethanol (denatured) and filtered to remove (numerous) particles. 10 mL of this solution in 7.5 L de-ionized water provided a concentration of 2.5×10^{-6} M. The thymol blue solution appears to change color slightly

over the course of a few days, and it is recommended that it be prepared close to the time of use.

B. Mixing Experiments and Apparatus

A simple jet mixing tank (30 cm inside diameter, 136 cm high, 1 cm ports 2.5 cm. from the bottom, 4 ports at 90 degrees) was used for developmental tests with the DISMT system. The pumping/mixing system consisted of two channels, each with a 2.2 gal reservoir, pump, recycle loop and valve, and flow meter and valve. Flow rates up to 8 L/min could be achieved. The mixed fluid in the tank could be drained back into the reservoirs for reuse. In a typical test, 6 L of the acidic (red) solution was pumped into the mixing tank, and then 6L of the basic (blue) solution was pumped into the mixing tank. The entire procedure was videotaped in color from the side. Each video sequence included a few seconds taping of a Color Checker®, a test pattern of 24 standard colors, to allow subsequent standardization of video images^[27] (Edmond, 1999). Figure 3 shows a schematic diagram of the mixing apparatus.

Figure 3

C. Preparation of Solutions to be Mixed

A program was prepared to accept input for a particular experiment (volumes to be mixed, δ , desired concentrations of indicators, temperature, ionic strengths, etc.), solve Equation 3 under various inputs, and provide output to the user. The program calculates the amounts of indicator solutions to be added, the initial pH's, the amounts of strong acid/base to be added, and the composition of the test solutions. It also estimates the precision with which a color change is associated with a particular δ .

The initial strategy was to use this program to calculate the desired initial pH's, carefully, calibrate the pH meter and electrode, and to add acid (or base) dropwise to adjust the pH within ± 0.02 pH units. However, it was found that many effects must be accounted for in order to *measure* the pH to this accuracy and precision. (calibration curve, ionic strengths, sodium ion effects, temperature, etc), and reliable operation of the DISMT method could not be achieved. The effective strategy was to use a program to calculate the initial pH's and the amounts of strong acid/base needed to achieve them. A colorimetric procedure, described in the following paragraph, was then used iteratively to set the pH of the base solution relative to that of the acid solution. Once this simple colorimetric setup test was satisfied, satisfactory performance with the full scale mixing experiment was reliably achieved.

In order to set up an experimental run, the calculated amounts of both indicators were added to both reservoirs. By dropwise addition of dilute HCl/KOH the pH in both reservoirs was adjusted to 7.0 ± 0.5 . The calculated amounts of 0.100 N HCl (KOH) were added to the acid (base) reservoirs, respectively. Three 5.0 mL aliquots were pipetted into 12 mL vials, and three calculated volumes (V_{red} , V_{yellow} , and V_{green}), corresponding to mixing fractions of $f = (1-5*\delta)*f_{\infty}$, f_{∞} , and $(1+5*\delta)*f_{\infty}$, were added to the vials, respectively. If the relative pH's were correct, the three vials showed balanced

red/yellow/green colors (almost like a traffic light). If the base solution was not sufficiently basic, the yellow appeared orange or orange/red. If the base solution was too basic, the yellow appeared green or blue/green. Balance of the optical depth of the red, yellow, and green solutions seemed to provide the most sensitive test. The best sensitivity was achieved when the solutions were viewed down the axis of the vial rather than across the vial, *i.e.*, at the maximum optical depth. Figure 4 shows a sequence of such tests including a well-balanced red/yellow/green sequence, which has been described as a “traffic light”. It is best to conduct the mixing run within 30 minutes of adjustment of the concentrations.

Figure 4

IV. Results and Discussion

A. Demonstration Mixing Experiment Using DISMT

Figure 5 shows a sequence of images obtained for a test mixing run with the DISMT system. The system was prepared as described in the previous sections, including balancing of the relative concentrations of the acid and base solutions with the “traffic light” technique. 6.0 L of the acid solution (red) was pumped into the tank and allowed to sit for approximately one minute. Then 6.0 L of the base solution (blue) was pumped into the tank, and the valve was closed. The valve on the base jet side was opened to full as quickly as possible, and once a little less than 6 L had been pumped, it was closed off as quickly as possible. In the first 60 seconds, there is very little change in the color, although with careful examination it is possible to see portions of the blue jet which have not yet completely reacted with the bulk red solution. In image (f), at 73 seconds, a base-rich zone at the lower left corner appears. In image (g), at 83 seconds, the base-rich zone has grown, and a zone of liquid with an orange and yellow color (mixing fraction near f_{∞}) appears across the top of the liquid. In image (h), at 93 seconds, the mixing fraction for the liquid in the upper right corner of the tank is in the “mixed within tolerance” zone, the liquid in the center of the tank is still acid, and the base-rich zone remains at the lower left corner. In images (I), (j) and (k), there is no more flow from the jet, and the liquid in the tank slowly evolves toward a homogeneous mixture with final mixing fraction f_{∞} , with substantial zones of green and orange color (which are actually reasonably well mixed, *i.e.*, $0.05 < \delta < 0.14$, see Section IV.C.) Image (l) was taken after the tank had been manually stirred. It shows the yellow color which is characteristic of the “mixed within tolerance” DISMT design. [Note: In these and other sequences of images, the relative times are accurate, but there may be an error of as much as 5 seconds in the absolute time.]

Figure 5

B. Comparison of DISMT with One Indicator Acid Base Methods

The range of interpretable colors shown in the Figure 5 DISMT color sequence can provide substantial semi-quantitative information. However, DISMT is somewhat more complex to carry out than standard one-indicator methods, and it is worthwhile to compare DISMT mixing results with those obtained with one-indicator methods.

Three comparisons were carried out. The volumes were the same as in the DISMT demonstration. In the first two, the standard DISMT procedure was used, except that no methyl red was added to the reservoirs. The concentration of the base solution relative to that of the acid solution was adjusted using the “traffic light” balancing (without the red). In the third, phenolphthalein (red in base, colorless in acid) was used as the only indicator (6×10^{-6} M in each reservoir), and the concentration of the base solution relative to that of the acid solution was adjusted as in the “traffic light” balancing. The middle vial was clear. Figure 6 shows selected images from the one indicator mixing experiments. In the left column, the acid (yellow) solution is injected from the left into the base (blue) solution. The zones which have $\text{pH} > \text{pK}_a(\text{TB}) = 9.2$ ($f_1 = 0.475$) appear blue; those with $\text{pH} < 9.2$ appear yellow. Very little information is provided about intermediate zones. The final solution is yellow as a consequence of the colorimetric balancing procedure used to set up the demonstration. In the center column the base solution is injected from the right into the acid solution. The same general pattern of blue ($\text{pH} > 9.2$) and yellow ($\text{pH} < 9.2$) is seen, and the final solution is yellow. In the right column, the acid (clear) solution is injected from the left into the base (magenta) solution. The clear liquid is difficult to identify through the magenta liquid, and the non-quantitative perception of color intensity by the human eye makes it difficult to identify regions of good mixing. Since the intensity of the magenta color increases continuously in the pH region 8- 9.8 [$\text{pK}_{1/2}(\text{phenolphthalein}) = 9.5$.²⁶], it is difficult to specify what the mixing fraction is at the transition from “weak magenta” to “clear”. The increase in information available with DISMT, relative to the one indicator methods, is substantial.

Figure 6

C. Interpretation of Color Change and Estimation of δ

Figure 2 seems to indicate that the color of the solution changes precisely at the mixing fractions f_1 and f_h . If this were so, then an observer could rigorously identify the yellow zone as “mixed within tolerance”. In reality, the changes take place over a range of pH (a phenomenon well known to students in quantitative analysis). In an attempt to estimate the uncertainty in identification of the “mixed within tolerance” zone, calculations of the error in estimation of f_1 and f_h (and consequently, δ) were carried out.

At $\text{pH} = \text{pK}_a(\text{MR})$, the solution appears orange, and at $\text{pH} = \text{pK}_a(\text{TB})$, the solution appears green. Many observers, however, will focus on the red and blue of the initial solutions and will identify the “mixed within tolerance” zone as “yellow only” rather than “orange through green (inclusive)”. The perceived δ for these observers is smaller than the design δ . Other observers will identify the “mixed within tolerance” zone as “neither red nor blue”, and their perceived δ will be larger than the design δ . Using Equation 3, mixing fractions were calculated for $\text{pH} = \text{pK}_a(\text{MR}) \pm \Delta\text{pH}$ and $\text{pK}_a(\text{TB}) \pm \Delta\text{pH}$. For $\Delta\text{pH} = 0.5$, the ratio of the acid to the base form of the indicator changes by about a factor of three from that at $\text{pH} = \text{pK}_a$. Other values of ΔpH could be used, but this one seems realistic. Figure 7 shows the results of such calculations for the actual DISMT system used in the demonstration mixing experiments, for which $\delta = 0.05$, $f_\infty = 0.50$, $f_1 = 0.475$, and $f_h = 0.525$. The leftmost, rightmost, and center zones would almost always be perceived as blue, red, yellow, respectively. An observer with a “yellow only” criterion would impose

the requirement that $5.5 < \text{pH} < 8.7$, which corresponds to $0.492 < f < 0.509$, or $\delta \cong 0.016$. An observer with a “neither red nor blue” criterion would impose the requirement that $4.5 < \text{pH} < 9.7$, which corresponds to $0.423 < f < 0.570$, or $\delta \cong 0.14$. The ambiguities described here would appear also in the determination of a mixing time.

Figure 7

The analysis described in the previous paragraph, taken in conjunction with the calculations shown in Figure 2, implies that use of higher concentrations of the acid-base indicators leads to more precise limits on the estimated value of δ . The indicators act as buffers and make the pH changes as a function of mixing fraction slower. However, the imposition of the requirements that $\text{pH}(f_l) = \text{pK}_a(\text{TB})$ and $\text{pH}(f_h) = \text{pK}_a(\text{MR})$ results in the use of stronger acid and base solutions. The net result is a higher value of the slope for $f \leq f_l$ and for $f \geq f_h$ (see Figure 2), and closer error limits on δ for an observer using the “neither red nor blue” criterion. The limits on δ for the “yellow only” criterion are virtually unchanged. A calculation analogous to that shown in Figure 7, but for $a_1 = a_2 = 1 \times 10^{-4} \text{ M}$, results in $\delta = 0.11$ for the “neither red nor blue” criterion.

B. Determination of Mixing Time Using DISMT

For many mixing experiments, the mixing time is defined as “the time for all of the liquid to become mixed within 5% (or 1%, or 0.1%) of the infinite time mixing fraction”. The DISMT system described in this paper enables an observer to examine the entire volume of the mixing region and, through observation of the colors within the system, to determine when all portions of the liquid are yellow, i.e., “mixed within tolerance”. The observer does not need to make prior judgements about where to place colorimetric probes (which may perturb the flows) or where to place the PLIF laser sheet. The concentration information which DISMT provides is semi-quantitative but incisive: the yellow color is the region in which the liquids are “mixed within tolerance”. The mixing time is unambiguously the time to achieve a uniform yellow color.

The colorimetric DISMT system is designed for “engineering insight” experiments. It is cheap and simple, with low toxicity reagents, and the mixed liquids can be drained back into the reservoirs, the acid and base concentrations easily readjusted, and the same reagents reused.

DISMT is direct, readily used, and specific for determination of the mixing time for molecular level mixing. It should be evaluated as a potential standard method for use by research scientists/engineers and by both purchasers and vendors of mixing equipment.

C. Future Work

In some cases, spatially precise information about the effectiveness of mixing is required, as for example, in the region near the tip of an impeller blade. For this situation and other such needs, a PLIF version of DISMT is under development: a characteristic color of fluorescence will identify the regions in which the liquids are “mixed within tolerance”. In addition many mixing problems involve liquids with viscosities

substantially higher than the viscosity of water. There appears to be no fundamental limitation in the DISMT chemistry which would conflict with the addition of appropriate polymeric viscosity enhancers, and thus it is anticipated that DISMT will be adapted for such uses also.

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VI. Disclaimer

The material presented in this paper is believed to be accurate. However no warranty is given or implied, and The Dow Chemical Company assumes no responsibility for its use by others.

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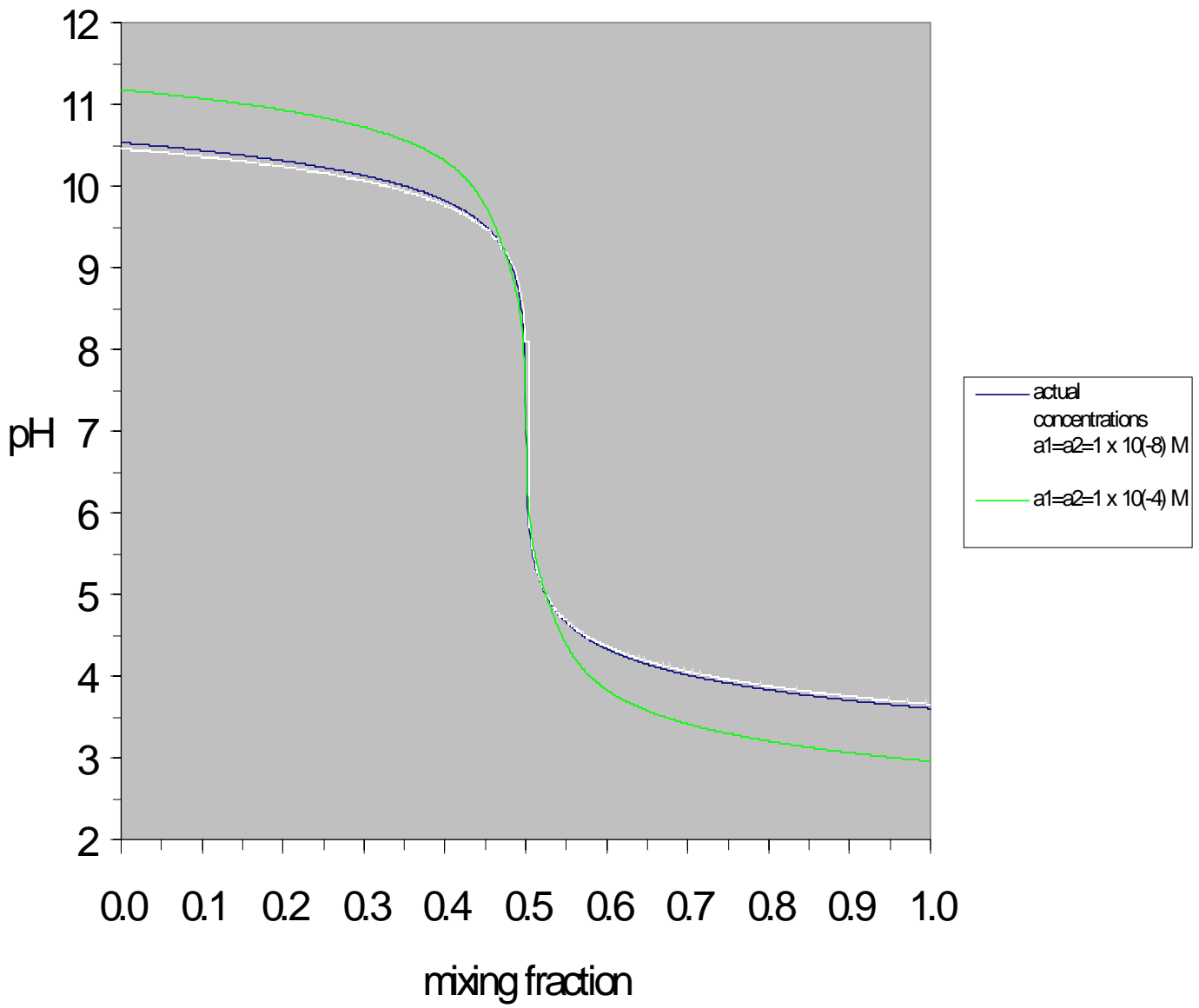
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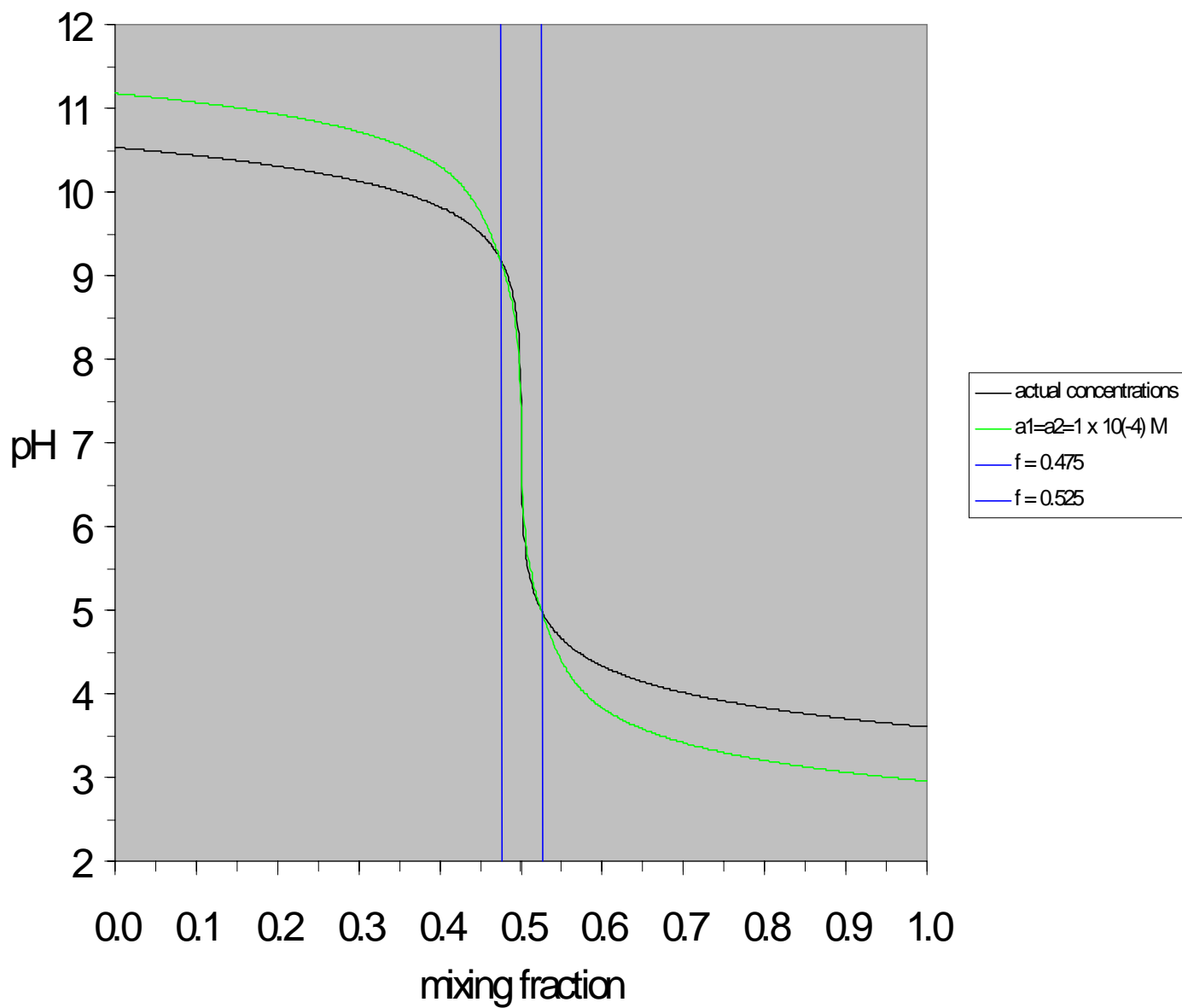
[27.] *Catalog*, Edmund Scientific Company, Barrington, NJ, item #H37756 (1999). Color Checker® is a trade designation of the GreyttagMacbeth™ Company.

Figure Captions

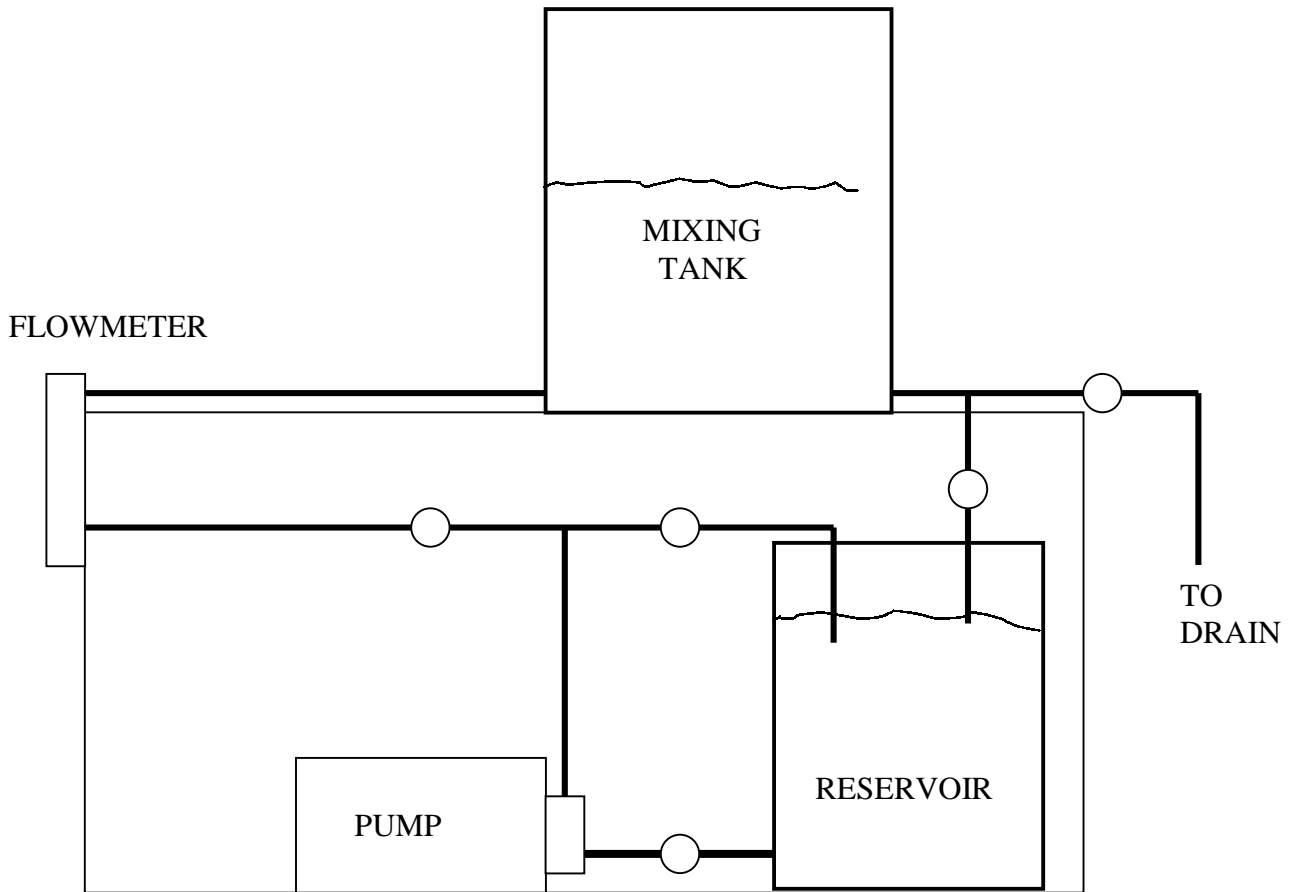
1. pH versus mixing fraction f
2. pH versus mixing fraction. Vertical lines are the values of f_l and f_h ($\text{pH} = \text{pK}_a$). In a ideal DISMT system, for $f < f_l$, the solution is blue; for $f_l < f < f_h$, yellow; and for $f > f_h$, red.
3. Schematic view of mixing apparatus (side view, only one reservoir/pump/flowmeter system is shown)
4. Colors obtained in colorimetric pH balance procedure (traffic light). (a) base concentration is significantly weak compared to the acid solution, column, (b) base concentration is modestly weak, (c), correct balance, (d), base concentration is modestly strong, and (e) base concentration is significantly strong.
5. Jet mixing sequence obtained with DISMT method. Time is in seconds after the start of the mixing flow (jet is from the right)
6. Jet mixing sequences obtained with one indicator methods. Time is in seconds after the start of the mixing flow. For the mixing of acid (yellow) solution into base (blue) [left column] and for the phenolphthalein mixing [right column], the jet is from the left; for the mixing of base (blue) into acid (yellow) [center column] the jet is from the right.
7. Estimation of δ for $\Delta\text{pH} = 0.5$. $a_1 = 5.0 \times 10^{-6} \text{ M}$; $a_2 = 2.5 \times 10^{-6} \text{ M}$. Vertical lines are the values of the mixing fraction which correspond to $\text{pH} = \text{pK}_a \pm \Delta\text{pH}$.



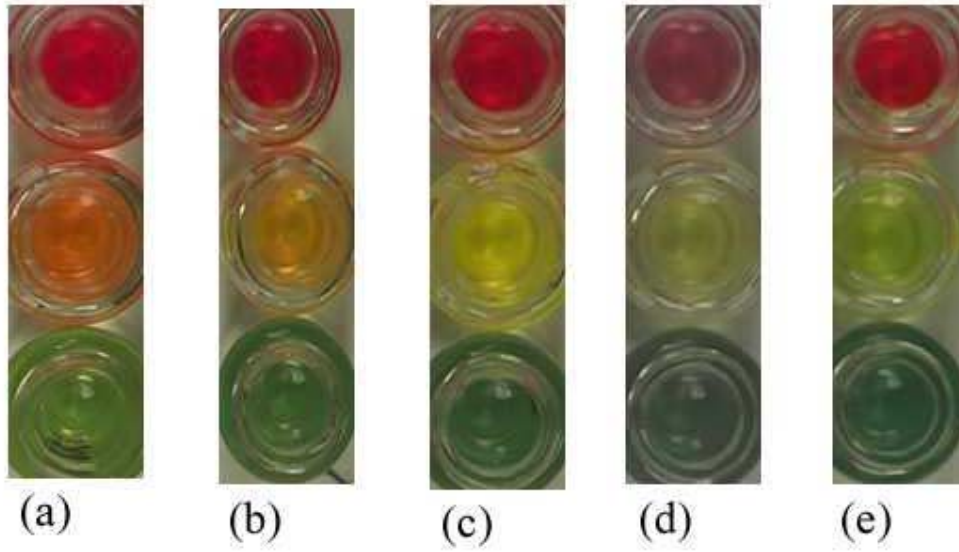
DISMT-Melton-FIGURE 1



DISMT-Melton-FIGURE 2



DISMT-Melton-Figure 3



DISMT-Melton-FIGURE 4



(a) filling



(b) $t = 0$



(c) $t = 32$



(d) $t = 53$



(e) $t = 63$



(f) $t = 73$



(g) $t = 83$



(h) $t = 93$



(i) $t = 103$



(j) $t = 113$



(k) $t = 121$



(l) stirred

DISMT-Melton-FIGURE 5



(a) filling



(e) filled



(i) filled



(b) $t = 63$



(f) $t = 50$



(j) $t = 73$



(c) $t = 73$



(g) $t = 60$



(k) $t = 83$



(d) $t = 83$

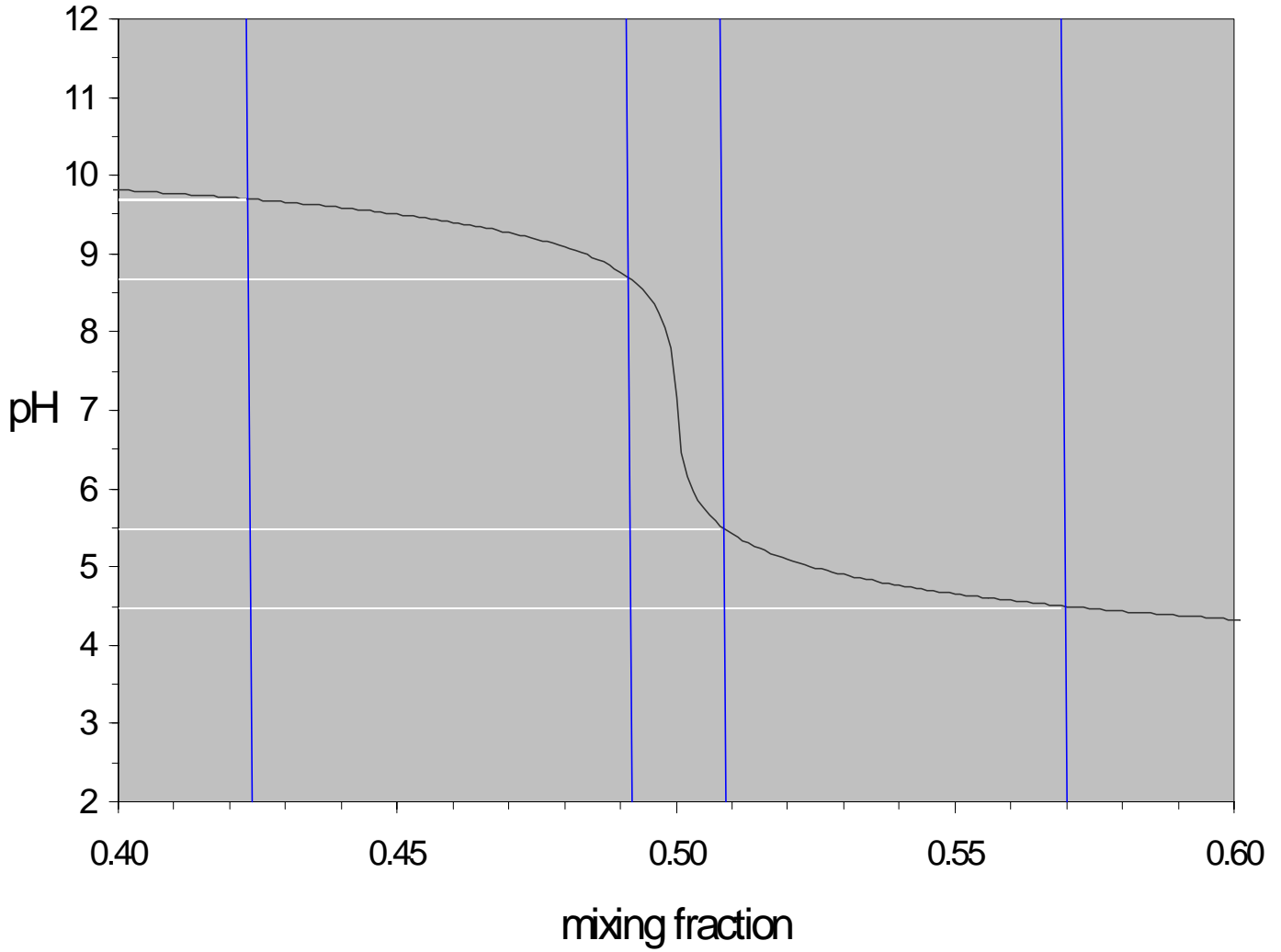


(h) $t = 70$



(l) $t = 93$

DISMT-Melton-FIGURE 6



DISMT-Melton-FIGURE 7