METHYLENE BLUE DOPED SOL-GELS: PREPARATION AND APPLICATION AS FIBER-OPTIC FLUORESCENCE SENSORS

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ABSTRACT

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The goal of this thesis project was to create a Methylene Blue (MB) doped sol-gel fiber-optic fluorescence sensor. Ideally this sensor would be capable of detecting changes in sulfite concentration in solution continuously and reversibly.

In aqueous solution, MB, a redox indicator, is converted from a bright blue color to the colorless leuco-MB species upon exposure to sulfite or other reducing agents. This reaction is reversible in the presence of an oxidizing agent. Therefore, if MB can be immobilized properly, it would make a suitable reversible indicator for the sulfite anion in solution.

The method of MB immobilization employed in this project was the sol-gel method. Organic solutes can be physically entrapped in sol-gels without being altered chemically. In this project, sol-gels were prepared by the hydrolysis and condensation of either tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS).

MB doped sol-gels were prepared using both TMOS and TEOS as precursors. Leaching of MB from these sol-gels does not appear to occur in neutral aqueous solution. The MB doped sol-gels prepared are responsive to the sulfite ion in solution; however, they are significantly less responsive to oxidizing agents. Blue MB is not readily regenerated from leuco-MB within the sol-gels. Moreover, the MB converts to the colorless leuco-MB form within the sol-gels over time even in the presence of oxidizing agents. Hence, this system requires further fundamental study before it can be used in the preparation of a reusable sol-gel fiber-optic fluorescence sulfite sensor. This system, however, is currently suitable for use as a disposable sulfite sensor.

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CHAPTER 1

INTRODUCTION

The overall goal of this project was to prepare an inexpensive SO_3^{2-} sensor using optical fibers and sol-gel technology. The project focused on the entrapment of Methylene Blue within silica-based sol-gels and the properties of these sol-gels.

1. FIBER OPTIC SENSORS

A sensor is a device that can record a physical parameter or the concentration of a chemical species continuously and reversibly. The ideal sensor will take a measurement within a few seconds and can be immersed directly into the sample of interest. Some examples of sensors are mercury thermometers, pH glass electrodes, non-bleeding pH paper strips, polarographic electrodes, thermistors and conductance sensors. A major advantage of sensors as compared to other methods is that they do not require the operations of sampling, addition of reagent, or dilution which introduce error into other analytical measurements. [1]

One class of sensors involves the use of optical fibers. Optical fibers employ the phenomenon of total internal reflectance to allow the transmission of light over large distances (typically 1 m to 100 m). An optical fiber consists of a core of refractive index n_1, a cladding with a lower refractive index, n_2, and a protective jacket (Figure 1-1). Light entering an optical fiber within an acceptance cone is transmitted by the fiber. The half angle of the acceptance cone for an optical fiber, α, is defined as:

$$\alpha = \sin^{-1}[(n_1^2-n_2^2)^{1/2} / n_o] \qquad (1)$$

where n_1 is the core refractive index, n_2 is the refractive index of the cladding and n_o is the refractive index of the outer medium. When the outer medium is air, $n_o = 0$. The range of angles for which light may enter an optical fiber and be transmitted is often

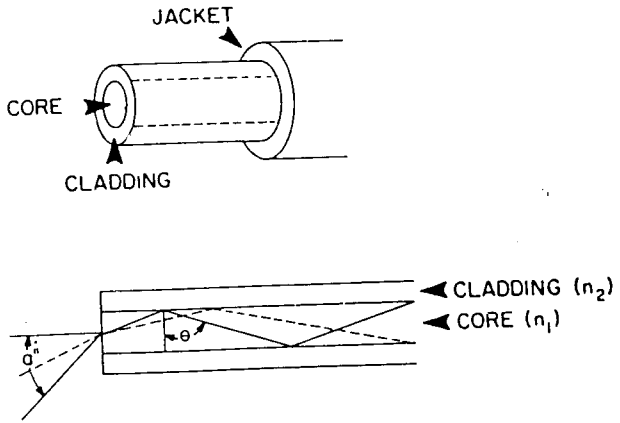


Figure 1-1. Top: Schematic of an optical fiber. Bottom: Path of light through an optical fiber.

Reprinted from [1].

described in terms of the numerical aperture (NA). The relationship between NA and α is illustrated in Equation 2 below. [1]

$$NA = n_o \sin \alpha \qquad (2)$$

The class of fiber-optic sensors can be subdivided into three "generations" of sensors. In a first-generation fiber-optic sensor, an analyte with an intrinsic optical property provides analytical information directly and the optical fiber serves only to transmit the optical signal of the analyte. First-generation sensors are also referred to as bare-ended or plain fiber sensors. [1]

Many analytes of interest, however, do not have an intrinsic optical property that can directly provide analytical information. In these cases, fiber sensors based on immobilized indicators can often be employed. These types of fiber sensors are classified as second-generation fiber-optic sensors. For these sensors, a change in the analyte will produce an optical change in an immobilized indicator. This optical change can be transmitted by an optical fiber and then measured. [1]

When an appropriate indicator is unavailable for a particular analyte, third-generation fiber optic sensors must be employed. This is commonly the case for biomolecules. Third-generation fiber-optic sensors consist of a second-generation sensor coupled to a reaction. In other words, for third-generation fiber-optic sensors, the analyte of interest is reacted with another molecule and the progress of the reaction is monitored by measuring either the consumption of reactant (other than the analyte of interest) or the formation of a product using a second-generation fiber-optic sensor. [1]

This project focused on the preparation of a second-generation fiber-optic sensor with Methylene Blue as the immobilized indicator.

2. METHYLENE BLUE (MB)

Methylene Blue (MB) has several applications, including its use as a redox indicator and as a cationic dye in the ion-pair extraction of colorless anions [2]. MB also has several biological applications. These include use as a biological stain, as an antiseptic in veterinary medicine and as an antidote for cyanide poisoning in humans and animals [3].

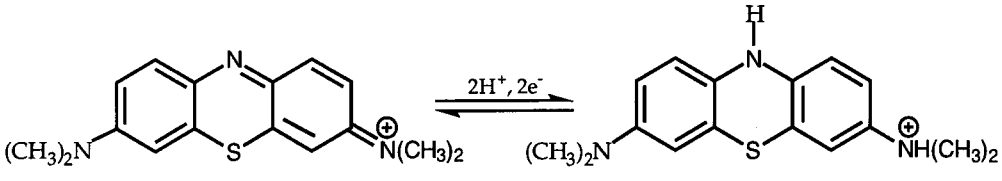
MB commonly exists in a hydrated chloride salt form with a molecular formula of $C_{16}H_{18}ClN_3S{\cdot}3H_2O$ (molecular weight = 373.90). This salt, also called 3,7-bis(dimethylamino)-phenazothionium chloride, exists as either a dark green odorless crystal with a bronze luster or as a crystalline powder. It is soluble in water (4g/100mL), ethanol (1.5g/100mL) and chloroform, but is insoluble in ether. [2]

As mentioned earlier, MB has frequently been used as a redox indicator. In aqueous solution, MB appears blue in color and absorbs maximally at approximately 661 nm [3]. In the presence of a reducing agent, MB is converted to the colorless leuco-MB (Methylene White) through the reaction illustrated in Figure 1-2 on the following page. This reaction is reversible over a pH range of 1 to 13. The reverse reaction will occur spontaneously when leuco-MB is exposed to O_2 or when leuco-MB is in the presence of light and the absence of air. [2]

The sulfite anion, SO_3^{2-}, is an example of a reducing agent that will react with MB to form leuco-MB. The relevant reduction reaction and potential for SO_3^{2-} are displayed below [4].

$$SO_4^{2-} + H_2O + 2e^- \Leftrightarrow SO_3^{2-} + 2OH^- \qquad E^\circ = -0.93\ V \qquad (3)$$

H_2O_2, $Cr_2O_7^{2-}$, IO_3^- and NO_3^- are oxidizing agents that can be used to convert leuco-MB to MB. The reduction reactions and potentials for these species are shown in Equations 4, 5, 6 and 7 [4].



MB (blue)

leuco-MB (colorless)

Figure 1-2. Reversible reaction of MB to leuco-MB (E = 0.532 V at T = 30°C). [2]

$$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O \qquad E^\circ = 1.776\ V \qquad (4)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \Leftrightarrow 2Cr^{3+} + 7\ H_2O \qquad E^\circ = 1.36\ V \qquad (5)$$

$$IO_3^- + 5H^+ + 4e^- \Leftrightarrow HOI + 2H_2O \qquad E^\circ = 1.154\ V \qquad (6)$$

$$NO_3^- + 3H^+ + 2e^- \Leftrightarrow HNO_2 + H_2O \qquad E^\circ = 0.940\ V \qquad (7)$$

Since blue MB is converted to colorless leuco-MB in the presence of SO_3^{2-} and can be regenerated in the presence of an oxidizing agent, MB could serve as a reversible indicator for a SO_3^{2-} sensor if immobilized properly.

3. SOL-GELS

The sol-gel process provides a means by which organic molecules can be trapped within an inorganic matrix under conditions of low temperature. Sol-gel processing involves the hydrolysis and condensation of metal or semi-metal alkoxides. The alkoxides most commonly used for sol-gel processing are TMOS [tetramethoxysilane, $(CH_3O)_4Si$] and TEOS [tetraethoxysilane, $(CH_3CH_2O)_4Si$], though other alkoxides, including tetraisopropoxytitanium and triisopropoxyaluminum, have also been employed in the sol-gel process [5].

There are three distinct phases in sol-gel processing: "sol" formation, gelation, and xerogel formation [6]. The hydrolysis and condensation of the alkoxide precursors produces a colloidal suspension called the "sol". As the interconnection between the particles of the "sol" increases, the viscosity of the "sol" also increases until a gel is formed [7]. The xerogel, or dry gel, is then produced upon additional drying [6]. The sol-gel process is typically used to form large monolithic glasses, fibers and thin films [6].

The progressive formation of a solid sol-gel matrix from the "sol" allows for a convenient means of entrapping organic molecules within this matrix. Figure 1-3 illustrates a dopant, protein molecules in the present case, being added to the "sol". As the sol-gel evolves, its increased networking causes the dopant molecules to become entrapped in the sol-gel. [7]

The average pore size and distribution of a sol-gel are affected by several different process parameters. These include temperature, pH, precursor molar ratios and hydrolysis time [5]. Of these, pH and precursor molar ratios appear to have the most significant effect on pore size and distribution in a sol-gel [5].

Immobilization of molecules within a sol-gel matrix has several advantages to conventional methods of immobilization. These conventional methods include covalent binding, physical adsorption, and cross-linking to a suitable carrier matrix [7]. Leaching and tedious preparation procedures are typical problems associated with the conventional methods of immobilization. Also, these methods of immobilization often cause the activity of the immobilized species to be substantially reduced. For example, MB has previously been electrostatically immobilized [8]. The electrostatically immobilized MB, however, is not converted to leuco-MB in the presence of SO_3^{2-}.

There is a significant amount of water trapped within the pores of a sol-gel matrix even in the dry xerogel form. This water provides an essentially aqueous environment for dopant molecules. As a result, the structure and activity of these dopant molecules is not affected significantly, as in conventional methods. Also, entrapment of a dopant molecule within a sol-gel matrix is independent of the functionalities on the molecule. This is not the case in the conventional methods of immobilization. [7]

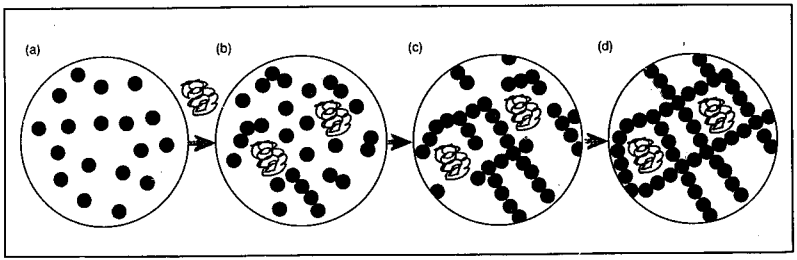


Figure 1-3. Entrapment of protein in a silicate sol-gel matrix.

Reprinted from [7].

Leaching can also be prevented by the use of sol-gel processing. Large molecules can be trapped within the pores of a sol-gel while, at the same time, smaller molecules are capable of flowing through these pores. This allows the encapsulated dopant molecules to react with analyte molecules. [7]

Sol-gels are transparent to light in the visible region and in much of the ultraviolet region of the spectrum [7]. Sol-gels also have low intrinsic fluorescence [5]. These sol-gel features allow the optical properties of dopant molecules to be monitored spectroscopically.

Other advantages of sol-gels include their physical rigidity, high abrasion resistivity, chemical inertness, and high biogradational, photochemical and thermal stability. The ease of sol-gel processing is also a major benefit of this immobilization method. [5]

Despite its numerous advantages over conventional methods, sol-gel processing does have some significant drawbacks. Sol-gels are typically fragile and will dissolve in solutions of high pH. Also, because of their high gelation temperatures, sol-gels are often difficult to mold. [5]

Sol-gels have previously been doped with active protein molecules (ex. glucose oxidase, hemoglobin, manganese myoglobin), polymers (ex. polymethyl methacrylate), and semiconductors (ex. titanium oxides, CdS, ZnS, CdTe), to name a few. These doped sol-gels have typically been used in fiber-optic sensors and in electroanalytical applications. [5] In this project MB was employed as the dopant molecule.

4. MB DOPED SOL-GEL FIBER OPTIC SENSORS

The goal of this research project was to create a fiber optic sensor capable of detecting changes in SO_3^{2-} concentration in solution. A silica sol-gel doped with MB

was to be coated on the tip of a fiber optic sensor. Optical changes in this sol-gel thin-film, resulting from the reduction of MB to leuco-MB in the presence of SO_3^{2-}, could then be monitored, and these optical changes could be related to the concentration of SO_3^{2-} in solution.

CHAPTER 2

PREPARATION OF SOL-GELS

1. PREPARATION OF PRE-SOL-GEL MIXTURES

A. Preparation of TEOS Pre-Sol-Gel Mixture [6]: The preparation of the TEOS pre-sol-gel mixtures employed in this project involved the mixing of TEOS (11.2 mL of 99+%, purchased from Aldrich), deionized water (1.8 mL), ethanol (6.05 mL of 95%) and HCl (8 μL of 1.00 M). The mixture is stirred uncovered at room temperature, allowing for the hydrolysis of the TEOS.

When the ingredients of the T re-sol-gel mixture are first mixed, some clear solid material is observed floating throughout the mixture. This solid material dissolves with additional stirring, leaving the TEOS pre-sol-gel mixture clear, colorless and homogeneous. The TEOS pre-sol-gel mixture becomes increasingly viscous with increased hydrolysis time and dries to form a clear, colorless, glassy solid after approximately six days of hydrolysis.

B. Preparation of TMOS Pre-Sol-Gel Mixture [6]: The preparation of the TMOS pre-sol-gel mixture is similar to that for the TEOS pre-sol-gel mixture. TMOS (7.38 mL of 99+%, purchased from Aldrich), deionized water (1.8 mL), ethanol (5.75 mL of 95%) and HCl (8μL of 1.00 M) are mixed. The mixture is stirred uncovered at room temperature, allowing for the hydrolysis of the TMOS.

The observations for the TMOS pre-sol-gel mixture are very similar to those for the TEOS pre-sol-gel mixture, the only major difference being the rate of solidification. The TMOS pre-sol-gel mixture solidifies to form a clear, colorless glassy solid after approximately three days of hydrolysis.

2. PREPARATION OF MB-MID-DOPED SOL-GELS

A. Preparation of TEOS MB-Mid-Doped Sol-Gels [6]: In the procedure for the preparation of TEOS MB-mid-doped sol-gels, one- to five-day hydrolyzed TEOS pre-sol-gel mixture is added to pH 6.0 phosphate buffer (0.1 M). MB, and in some cases Triton-X, is then stirred into this mixture. The resulting "sol" is dried uncovered at room temperature and eventually undergoes gelation and xerogel formation.

After several days of drying, these TEOS MB-mid-doped sol-gels appear solid and glass-like. Cracking of the sol-gels during the drying period is prevalent as is shrinking of the sol-gels. The dry xerogels appear blue in color and the intensity of this blue color increases with increasing amounts of added MB.

The ingredients used to prepare the TEOS MB-mid-doped sol-gels are listed in Table 2-1 below.

Table 2-1: Ingredients for the Preparation of TEOS MB-Mid-Doped Sol-Gels

Sol-Gel	Number of Days TEOS Pre-Sol-Gel Mixture Hydrolyzed	Amount of TEOS Pre-Sol-Gel Mixture Added (mL)	Amount of pH 6.0 Phosphate Buffer (0.1 M) Added (mL)	Amount of MB Added (nmol)	Amount of 0.2% Triton-X Added (μL)
Mid-1E	5	2.50	1.25	7.5	0
Mid-2E	1	2.50	1.25	9.0	20
Mid-3E	3	2.50	1.25	9.0	100
Mid-4E	2	13.3	6.67	36.0	0
Mid-5E	1	2.50	1.25	4.0	0
Mid-6E	1	2.50	0.938	4.0	0
Mid-7E	1	2.50	0.625	4.0	0
Mid-8E	1	2.50	0.313	4.0	0

B. Preparation of TMOS MB-Mid-Doped Sol-Gels [6]: The procedure for the preparation of TMOS MB-mid-doped sol-gels is similar to that for the TEOS MB-mid-doped sol-gels. The only change from the TEOS MB-mid-doped sol-gel preparation

procedure is that hydrolyzed TMOS pre-sol-gel mixture is used in place of TEOS pre-sol-gel mixture.

The dry TMOS MB-mid-doped sol-gels appear solid, blue and glass-like. The extent of the blue color in the sol-gels is proportional to the amount of MB added during the preparation procedure. Cracking and shrinking of the sol-gels during the drying period is often observed, as is the case for the TEOS mid-doped sol-gels.

The ingredients used in the preparation of the TMOS MB-mid-doped sol-gels are listed in Table 2-2 below.

Table 2-2: Ingredients for the Preparation of TMOS MB-Mid-Doped Sol-Gels

Sol-Gel	Number of Days TMOS Pre-Sol-Gel Mixture Hydrolyzed	Amount of TMOS Pre-Sol-Gel Mixture Added (mL)	Amount of pH 6.0 Phosphate Buffer (0.1 M) Added (mL)	Amount of MB Added (nmol)
Mid-1M	1	2.50	1.25	7.5
Mid-2M	1	2.50	1.25	5.0

C. Preparation of TEOS MB-Mid-Doped Monolith Sol-Gels: The procedure for the preparation of the TEOS MB-mid-doped monoliths is similar to that described for the preparation of MB-mid-doped sol-gels. Hydrolyzed TEOS pre-sol-gel mixture, phosphate buffer (pH 6.0, 0.1 M) and MB are added together in a polystyrene cuvette. The plastic cuvette is then sealed with parafilm and inverted several times to insure the mixing of the contents of the cuvette. The sol-gel in the plastic cuvette is then allowed to dry at room temperature. A table listing the ingredients used to prepare the MB-mid-doped sol-gel monoliths can be seen on the following page (Table 2-3). Observations concerning the progress of the TEOS sol-gel monoliths during the drying process are described in Chapter 3.1.

Table 2-3: Ingredients for Preparation of MB-Mid-Doped Sol-Gel Monoliths

Sol-Gel	Number of Days TEOS Pre-Sol-Gel Mixture Hydrolyzed	Amount of TEOS Pre-Sol-Gel Mixture Added (mL)	Amount of pH 6.0 Phosphate (0.1 M) Buffer Added (mL)	Amount of MB Added (nmol)
Monolith-1E	1	2.50	1.25	0.5
Monolith-2E	1	2.50	1.25	1.5
Monolith-3E	1	2.50	1.25	3.0
Monolith-4E	1	2.50	1.25	5.0
Monolith-5E	1	2.50	1.25	7.5
Monolith-6E	2	2.50	1.25	0.5
Monolith-7E	2	2.50	1.25	1.5
Monolith-8E	2	2.50	1.25	3.0
Monolith-9E	2	2.50	1.25	5.0
Monolith-10E	2	2.50	1.25	7.5

3. PREPARATION OF MB-POST-DOPED SOL-GELS

A. Preparation of TEOS MB-Post-Doped Sol-Gels: MB-post-doped sol-gels are prepared by first mixing TEOS pre-sol-gel with pH 6.0 phosphate buffer (0.1 M) and, in some cases, Triton-X. The resulting mixture is allowed to dry uncovered at room temperature and eventually undergoes gelation and xerogel formation. The non-doped, colorless, glass-like TEOS sol-gels that result are soaked in MB solution. In all cases, except for the non-doped sol-gel pieces to which no buffer was added (Post-9E), MB was taken up into the sol-gel pieces from solution.

The resulting post-doped sol-gel pieces are solid, glass-like and blue in color. The MB solutions in which the non-doped sol-gel pieces are soaked become less blue as the sol-gel post-doping process takes place.

The ingredients used for the preparation of the non-doped sol-gels and the concentrations of the MB solutions in which the non-doped sol-gels were soaked are listed in Table 2-4 on the following page.

Table 2-4: Ingredients For The Preparation Of TEOS MB-Post-Doped Sol-Gels

Sol-Gel	Number of Days TEOS Pre-Sol-Gel Mixture Hydrolyzed	Amount of TEOS Pre-Sol-Gel Mixture Added (mL)	Amount of pH 6.0 Phosphate Buffer (0.1 M) Added (mL)	Amount of 0.2% Triton-X Added (μL)	Concentration of MB Solution Used to Post-Dope Sol-Gels (M)
Post-1E	5	2.50	1.25	0	1.00×10^{-4}
Post-2E	5	2.50	1.25	0	4.0×10^{-6}
Post-3E	3	2.50	1.25	100	1.00×10^{-5}
Post-4E	3	2.50	1.25	100	3 mL of 1.00×10^{-4} M
Post-5E	3	2.50	1.25	100	3 mL of 1.00×10^{-5} M
Post-6E	3	2.50	1.25	100	3 mL of 5.00×10^{-6} M
Post-7E	2	13.3	6.67	0	1.00×10^{-5}
Post-8E	1	2.50	0.625	0	1.00×10^{-5}
Post-9E	5-6	unknown	0	0	1.00×10^{-5}
Post-10E	1	≅1.5	1.25	0	1.00×10^{-5}
Post-11E	3	7.65	6.67	0	1.00×10^{-5}
Post-12E	1	13.3	6.67	0	1.00×10^{-5}

B. Preparation of TMOS MB-Post-Doped Sol-Gels: The preparation procedure for TMOS MB-post-doped sol-gels is very similar to that for the TEOS MB-post-doped sol-gels, the only difference being that TMOS pre-sol-gel mixture is used in place of TEOS pre-sol-gel mixture.

The TMOS post-doped sol-gels are also solid, glass-like and blue in color. The ingredients used to prepare the TMOS MB post-doped sol-gels are listed in Table 2-5 on the following page.

Table 2-5: Ingredients for the Preparation of TMOS MB-Post-Doped Sol-Gels

Sol-Gel	Number of Days TMOS Pre-Sol-Gel Mixture Hydrolyzed	Amount of TMOS Pre-Sol-Gel Mixture Added (mL)	Amount of pH 6.0 Phosphate Buffer (0.1 M) Added (mL)	Amount of 0.2% Triton-X Added (μL)	Concentration of MB Solution Used to Post-Dope Sol-Gels (M)
Post-1M	≅3	unknown	0	0	1.00×10^{-4}
Post-2M	1	2.00	1.00	0	1.00×10^{-5}
Post-3M	1	2.00	0.500	0	1.00×10^{-5}
Post-4M	1	2.00	0.250	0	1.00×10^{-5}
Post-5M	1	2.00	0.100	0	1.00×10^{-5}

4. PREPARATION OF TEOS SOL-GEL COATED SLIDES

The slides employed in this experiment were either white-water glass microscope slides or borosilicate glass cover slips (purchased from Fisher). In the preparation of TEOS sol-gel coated slides/slips, a sol is created by mixing hydrolyzed TEOS pre-sol-gel mixture and pH 6.0 phosphate buffer (0.1 M) in a petri dish. A glass slide/slip, washed either with acid and base (A) or with methanol (B), is added to the sol-gel mixture in the petri dish. The TEOS sol-gel mixture is swirled about the petri dish to ensure that the slide/slip is entirely covered by the sol-gel mixture. The slide/slip is then removed from the petri dish and clamped, either horizontally or vertically, to a ring stand. The sol-gel coated slide/slip is allowed to dry at room temperature. Some of the coated slides/slips were later soaked in MB solution in an attempt to MB-post-dope their sol-gel coatings.

A. Acid/Base Wash: Clean slides/slips were soaked in concentrated HNO_3 for approximately one hour. After being rinsed with deionized water, these slides were

transferred to a solution of 6 M NaOH for approximately one hour. The slides were then rinsed with deionized water and dried in an oven at approximately 100°C. The slides were removed from the oven and cooled to room temperature before they were dipped in sol-gel mixture. The ingredients used to create the sol-gel mixture(s) in which the microscope slides were dipped can be seen in Table 2-6 on the following page. Also listed in this table are the types of glass, times at which the slides were dipped (t = 0 when the phosphate buffer and pre-sol-gel mixture are first mixed), the position in which the slides were dried (horizontally or vertically) and the concentration of MB in which the sol-gel coated slides were soaked.

B. Methanol Wash [11]: Clean glass slides/slips were soaked in spectroscopy grade methanol (99.9%) for 20 to 60 minutes. These slides/slips were then removed from the methanol and dried in an oven overnight at 95°C. The slides/slips were cooled to room temperature before they were dipped in sol-gel mixture. Table 2-7 lists the parameters for the preparation of the TEOS sol-gel coated slides/slips that had been previously washed with methanol.

Table 2-6: Parameters for the Preparation of TEOS Sol-Gel Coated Microscope Slides, Acid/Base Wash

Name of Sol-Gel Coated Microscope Slide	Type of Slide Coated (White-Water Glass or Borosilicate Glass)	Number of Days TEOS Pre-Sol-Gel Mixture Hydrolyzed	Amount of TEOS Pre-Sol-Gel Mixture Added (mL)	Amount of pH 6.0 Phosphate Buffer (0.1 M) Added (mL)	Time Elapsed Before Slide Added to Sol-Gel Mixture (min)	Dried Vertically or Horizontally	Concentration of MB Solution Used to Post-Dope the Sol-Gels (M)
Slide-1AB	white-water	2	13.3	6.67	?	vertically	-
Slide-2AB	white-water	2	13.3	6.67	?	vertically	1.00×10^{-5}
Slide-3AB	white-water	2	13.3	6.67	?	horizontally	-
Slide-4AB	white-water	2	13.3	6.67	?	horizontally	-
Slide-5AB	white-water	2	13.3	6.67	≅5	vertically	1.00×10^{-5}
Slide-6AB	white-water	2	13.3	6.67	≅5	vertically	-
Slide-7AB	white-water	2	13.3	6.67	≅5	vertically	-
Slide-8AB	white-water	2	13.3	6.67	≅15	vertically	-
Slide-9AB	white-water	2	13.3	6.67	≅15	vertically	-
Slide-10AB	white-water	2	13.3	6.67	≅25	vertically	1.0×10^{-5}
Slide-11AB	white-water	2	13.3	6.67	≅25	vertically	-

Table 2-7: Parameters for the Preparation of TEOS Sol-Gel Coated Microscope Slides, Methanol Wash

Name of Sol-Gel Coated Microscope Slide	Type of Slide Coated (White-Water Glass or Borosilicate Glass)	Number of Days TEOS Pre-Sol-Gel Mixture Hydrolyzed	Amount of TEOS Pre-Sol-Gel Mixture Added (mL)	Amount of pH 6.0 Phosphate Buffer Added (mL)	Time Elapsed Before Slide Added to Sol-Gel Mixture (min)	Vertically or Horizontally Dried	Concentration of MB Solution Used to Post-Dope the Sol-Gels (M)
Slide-1MeOH	white-water	3	7.65	6.67	≅1	vertically	-
Slide-2MeOH	white-water	3	7.65	6.67	≅3	vertically	-
Slide-3MeOH	white-water	3	7.65	6.67	≅5	vertically	-
Slide-4MeOH	white-water	3	7.65	6.67	≅7	vertically	-
Slide-5MeOH	borosilicate	1	13.3	6.67	?	vertically	-
Slide-6MeOH	borosilicate	1	13.3	6.67	?	vertically	-
Slide-7MeOH	borosilicate	1	13.3	6.67	?	vertically	-
Slide-8MeOH	borosilicate	1	13.3	6.67	?	vertically	-
Slide-9MeOH	borosilicate	1	13.3	6.67	?	vertically	$\cong 10^{-4}$
Slide-10MeOH	borosilicate	1	13.3	6.67	≅5	vertically	-
Slide-11MeOH	borosilicate	1	13.3	6.67	≅10	vertically	-
Slide-12MeOH	borosilicate	1	13.3	6.67	≅15	vertically	1.0×10^{-5}
Slide-13MeOH	borosilicate	1	13.3	6.67	≅17	vertically	-

CHAPTER 3

RESULTS

1. MONOLITH PROGRESS

TEOS monoliths were prepared in polystyrene cuvettes with a parafilm seal (Chapter 2, 2C). The changes that occurred in these monoliths over time were observed and recorded. These observations are summarized in Table 3-1 on the following pages.

Throughout the rest of this text, "Non-aE" will refer to the Post-aE sol-gel, as defined in Chapter 2, before post-doping had occurred. For instance, the name Non-10E will be used for the Post-10E sol-gel before its addition to aqueous MB solution. The Non-10E sol-gel was dried uncovered in a vial that had a slightly concave bottom. After 2 days of drying, the sol-gel was solid, cylindrical, and in one piece. It was slightly "gummy" and there were a few tiny bubbles observed within the sol-gel. After 6 days of drying, the Non-10E sol-gel remained in one piece. The sol-gel was transparent but slightly cloudy and it had shrunk significantly. After 26 days of drying, aqueous MB (1.00×10^{-5} M) was added to the sol-gel piece. After approximately 10 seconds in the MB solution, the monolith began to crack. Cracking continued until the monolith had broken into several tiny pieces.

2. SHRINKING OF SOL-GELS

The volumes of the sol-gels prepared (Chapter 2) decreased during the drying period, without exception. The extent of this decrease in volume was difficult to measure in ordinary sol-gel batches because these batches typically split into smaller sol-gel pieces during the drying process. The volumes of the dry sol-gel monoliths, however, were not difficult to obtain. The dimensions of these monoliths were found using a ruler and the volumes were calculated accordingly. These measurements and calculations can be seen in Table 3-2. The data and calculations in Table 3-2 illustrate

Table 3-1: TEOS Monolith Progress

Sol-Gel	Observations
Monoliths-1E, 2E, 3E, 4E and 5E	After 3 days of drying, there were solid sol-gel pieces, rectangular in cross section, as well as some liquid sol-gel in each of the cuvettes. Several bubbles were seen throughout the solid pieces of sol-gel. ⇒ After 77 days, there were no significant changes observed in any of the sol-gels. The parafilm seals were removed from the cuvettes and replaced with lighter parafilm seals. ⇒ After 124 days, there were no significant changes observed in the sol-gels. The parafilm seals were again removed from the cuvettes and replaced with light parafilm seals.
Monolith-6E	After 1 day of drying, there was a solid sol-gel piece, rectangular in cross section, as well as some liquid sol-gel in the cuvette. Several bubbles were seen throughout the solid piece of sol-gel. ⇒ After 75 days, there was no significant change observed in the sol-gel. The parafilm seal was removed from the cuvette and replaced with a very light parafilm seal. ⇒ After 86 days, the sol-gel was completely solid and in two pieces. The pieces appeared clear and colorless and there were several small bubbles throughout them. The sol-gel had shrunk significantly. ⇒ After 105 days, the shrinking of the monolith was even more evident. ⇒ After 166 days, 1.0×10^{-5} M MB was added to one of the monolith halves drop-wise. The monolith half cracked into smaller pieces as more MB was added. Eventually, the entire monolith half had broken into very tiny pieces. Deionized H_2O was added drop-wise to the other monolith half. The monolith began to crack upon the addition of H_2O and continued to crack until the monolith half had broken into several tiny pieces.
Monolith-7E	After 1 day of drying, there was a solid sol-gel piece, rectangular in cross section, as well as some liquid sol-gel in the cuvette. Several bubbles were seen throughout the solid piece of sol-gel. ⇒ After 75 days, there was no significant change observed in the sol-gel. The parafilm seal was removed from the cuvette and replaced with a very light parafilm seal. ⇒ After 86 days, the sol-gel was completely solid and in one piece. The monolith appeared clear and colorless and there were several small bubbles throughout it. The sol-gel had shrunk significantly. ⇒ After 105 days, the shrinking of the monolith was even more evident. ⇒ After 127 days, aqueous 1.0×10^{-5} M MB was added to the monolith. Almost instantaneously the monolith began to crack into smaller pieces. Eventually, the monolith had broken down into hundreds of tiny sol-gel pieces.

Table 3-1: TEOS Monolith Progress (continued)

Sol-Gel	Observations
Monolith-8E	After 1 day of drying, there was a solid sol-gel piece, rectangular in cross section, as well as some liquid sol-gel in the cuvette. Several bubbles were seen throughout the solid piece of sol-gel.⇒ After 74 days, both solid and liquid sol-gel were still present in the cuvette. The contents of the cuvette were emptied into a beaker. The solid portion of the sol-gel was rectangular in cross section and in one piece. The surface of this monolith was "gummy" and the monolith was easily broken into smaller pieces. The sol-gel was allowed to dry uncovered overnight. It appeared opaque and white the next day. When touched with a spatula, the sol-gel crumbled into a white powder.
Monolith-9E	After 1 day of drying, there was a solid sol-gel piece, rectangular in cross section, as well as some liquid sol-gel in the cuvette. Several bubbles were seen throughout the solid piece of sol-gel. ⇒ After 122 days, there was no significant change observed in the sol-gel. The parafilm seal was removed from the cuvette and replaced with a lighter parafilm seal. ⇒ After 175 days, there was no significant change observed in the sol-gel. The parafilm seal was again removed from the cuvette and replaced with a very light parafilm seal. ⇒ After 182 days, the sol-gel appeared colorless, clear and completely solid. There were several bubbles throughout the sol-gel but not much shrinking had occurred. ⇒ After 195 days, the shrinking of the sol-gel was extensive.
Monolith-10E	After 1 day of drying, there was a solid sol-gel piece, rectangular in cross section, as well as some liquid sol-gel in the cuvette. Several bubbles were seen throughout the solid piece of sol-gel. ⇒ After 122 days, there was no significant change observed in the sol-gel. The parafilm seal was removed from the cuvette and replaced with a lighter parafilm seal. ⇒ After 175 days, there was no significant change observed in the sol-gel. The parafilm seal was again removed from the cuvette and replaced with a very light parafilm seal. ⇒ After 182 days, the sol-gel appeared colorless and clear. Most of the sol-gel was in the solid form, although some sol-gel remained in the liquid form. There were a few bubbles throughout the sol-gel and no shrinking was evident. ⇒ After 195 days, the monolith was completely solid, in two pieces, clear and colorless. The monolith pieces were not very uniform and their were bubbles and cracks throughout the sol-gel pieces. Shrinking of the sol-gel was extensive.

Table 3-2: Percent Shrinkage of Sol-Gels During the Drying Process

Sol-Gel	Initial Volume (Before Drying)	Dimensions of Dry Sol-Gel	Calculating Volume of Dry Sol-Gel	Calculating What Percent of the Initial Sol-Gel Volume is the Volume of the Dry Sol-Gel
Monolith-6E	3.76 mL	(rectangular in cross section) length = 0.5 cm width = 0.5 cm height = 1.9 cm	Volume = lwh V = (0.5 cm)(0.5 cm)(1.9 cm) *Volume = 0.4_8 cm^3 = 0.4_8 mL*	= final volume/initial volume * 100 = (0.4_8 mL)/(3.76 mL) * 100 = **1_3%**
Monolith-7E	3.77 mL	(rectangular in cross section) length = 0.5 cm width = 0.5 cm height = 1.83 cm	Volume = lwh V = (0.5 cm)(0.5 cm)(1.83 cm) *Volume = 0.4_6 cm^3 = 0.4_6 mL*	= final volume/initial volume * 100 = (0.4_6 mL)/(3.77 mL) * 100 = **1_2%**
Non-10E	≅2.8 mL	(cylindrical) diameter = 1.0 cm height = 0.2 cm	Volume = $\pi r^2 h$ V = π $(0.50\ cm)^2(0.2\ cm)$ *Volume = 0.1_6 cm^3 = 0.1_6 mL*	= final volume/initial volume * 100 = (0.16 mL)/(2.8 mL) * 100 = **$5._7$%**

clearly that significant shrinking of sol-gels does occur during the drying process. Note that more precise measurements could have been made using a micrometer.

3. MB-DOPED SOL-GELS IN DEIONIZED WATER

A. Color Changes in Sol-Gels: Several of the sol-gels prepared, including mid- and post-doped and TEOS and TMOS sol-gels, were soaked in deionized water for extended periods of time. These sol-gels are listed in Table 3-3. Also listed in Table 3-3 are the colors of these sol-gels at different time intervals during the soaking process. The intervals listed in the table do not represent the exact times at which the sol-gels changed colors because the sol-gels that were soaked in water were not examined daily. Instead, these times provide a rough estimate of the rate of color change in the sol-gels when soaked in deionized water.

It is evident from the data listed in Table 3-3 that there is a tendency for the MB-doped sol-gels to change from blue to colorless or near colorless when soaked in deionized water. The only sol-gels thus far that have not exhibited this behavior have been the Post-1M, 2M, 3M, 4M and 5M sol-gels.

B. Color Changes in Deionized Water: The color of the deionized water samples in which each of the sol-gels listed in Table 3-3 were soaked were examined during the soaking process. Each of these water samples appeared colorless throughout the soaking process. The water samples in which the Mid-1E (Trial 1), Mid-1E (Trial 2), Mid-2E, Mid-3E, Mid-4E, Mid-5E, Mid-6E, Mid-7E, Mid-8E, Post-5E, Post-6E, Post-7E, Post-8E and Post-1M sol-gels were soaked were examined for MB content using UV/visible absorption spectroscopy. The absorbance of each water sample was found using a Hewlett Packard 8452A diode array spectrophotometer. The absorbance readings were taken at 666 nm, near the absorbance maximum for MB.

Table 3-3: Sol-Gels in Deionized Water

Sol-Gel	Color of Sol-Gel Before Addition to H_2O	Length of Time Soaking in H_2O; Sol-Gel Color			
Mid-1E (Trial 1)	blue	7 days; much lighter blue in color than before addition to H_2O	20 days; hardly any of the original blue color remained	43 days; colorless	
Mid-1E (Trial 2)	blue	6 days; blue (no visible color change)	13 days; more dull blue in color than before addition to H_2O	35 days; colorless	
Mid-1E (Trial 3)	blue	15 days; only a faint blue tint to the sol-gel piece	74 days; colorless		
Mid-2E	blue	15 days; blue (no visible color change)	33 days; near colorless with a slight blue tint		
Mid-3E	aqua blue	10 days; aqua blue (no visible color change)	30 days; purple-blue	87 days; near colorless (possibly a slight blue tint)	119 days; colorless
Mid-4E	aqua blue	8 days; aqua blue (no visible color change)	31 days; colorless		
Mid-5E	bright blue	11 days; deep blue in color but slightly lighter blue than before addition to H_2O	46 days; very light blue		
Mid-6E	bright blue	11 days; bright blue	46 days; very light blue	82 days; near colorless with light blue-purple tint	
Mid-7E	bright blue	11 days; bright blue	46 days; bright blue	82 days; near colorless with light purple tint	

Table 3-3: Sol-Gels in Deionized Water (Continued)

Sol-Gel	Color of Sol-Gel Before Addition to H_2O	Length of Time Soaking in H_2O; Sol-Gel Color			
Mid-8E	bright blue	11 days; bright blue	46 days; light blue-purple	82 days; near colorless with light purple tint	
Mid-1M	blue	6 days; blue (no visible color change)	25 days; blue tint	48 days; colorless	
Post-1E	dark blue	94 days; blue in color but lighter blue than before addition to H_2O	126 days; light purple/lavender		
Post-5E	bright blue	58 days; bright purple-blue	90 days; bright purple-blue	112 days; light purple	145 days; light purple
Post-6E	bright blue	58 days; purple-blue	90 days; light purple-lavender	112 days; slight lavender tint	145 days; colorless
Post-7E	aqua blue	25 days; blue	56 days; light blue-purple	92 days; near colorless with light blue tint	
Post-8E	bright blue	11 days; bright blue	46 days; light blue-purple	82 days; purple	
Post-1M	dark blue	18 days; dark blue	41 days; dark blue	74 days; dark blue	110 days; dark blue
Post-2M	bright blue	5 days; bright blue	41 days; bright blue		
Post-3M	bright blue	5 days; bright blue	41 days; bright blue		
Post-4M	bright blue	5 days; bright blue	41 days; most of sol-gel was bright blue but some parts were colorless		
Post-5M	bright blue	5 days; bright blue	41 days; bright blue		

None of the water samples showed a significant absorbance value at 666 nm; therefore, MB was not detected in any of these samples.

4. CRACKING OF SOL-GELS IN AQUEOUS SOLUTION

It is well known that sol-gels prepared using TEOS or TMOS as alkoxide precursors often crack in aqueous solution [5]. The sol-gels that I prepared (Chapter 2) were consistent with this fact. The cracking behavior of several of the sol-gels that were prepared in aqueous solution is tabulated in Table 3-4.

It has been suggested that Triton-X could decrease the extent of sol-gel cracking in aqueous solution [5]. Triton-X was added to some of the sol-gels during the preparation procedure. As mentioned in Chapter 2, the Triton-X was added to the sol-gels when the pre-sol-gel mixture and pH 6.0 phosphate buffer were mixed. Whether Triton-X was added during the preparation of each sol-gel is indicated in Table 3-4.

5. SOL-GELS IN BASIC SOLUTION

A sol-gel piece from the Mid-1E batch that had been dried for 2 days was immersed in 6 M NaOH solution. After approximately two hours in this solution, the sol-gel appeared to have decreased in size. After soaking overnight in the 6 M NaOH solution, the piece of Mid-1E sol-gel had dissolved completely. Sol-gels prepared using TEOS, then, were observed to dissolve in basic solution as has been reported previously in the literature [5].

Sol-gel pieces from the Post-2M batch which had been dried for 61 days were immersed in 6 M NaOH solution. These sol-gel pieces did not dissolve when soaked in the basic solution for 2 days.

Table 3-4: Cracking of Sol-Gels in Aqueous Solution

Sol-Gel	Triton-X?	Length of Sol-Gel Drying Time	Aqueous Solution	Observations Upon Immersion of the Sol-Gel in the Specified Aqueous Solution
Mid-1E	No	4 days	0.1 M Na_2SO_3	sol-gel piece shattered into several (15-20) smaller pieces
Mid-2E	Yes (20 μL)	1 day	Deionized H_2O	sol-gel piece broke into several pieces
Mid-2E	Yes (20 μL)	14 days	Saturated Na_2SO_3	sol-gel remained in one piece
Mid-3E	Yes (100 μL)	4 days	Deionized H_2O	sol-gel piece shattered into several pieces
Mid-3E	Yes (100 μL)	4 days	Saturated Na_2SO_3	sol-gel piece shattered into several pieces
Mid-3E	Yes (100 μL)	12 days	Saturated Na_2SO_3	only a few (2-3) chips broke off of the sol-gel piece
Mid-4E	No	4 days	Deionized H_2O	after 10-15 seconds, the sol-gel piece began to break up into tiny sol-gel pieces; eventually, only small sol-gel pieces remained
Mid-4E	No	4 days	Saturated Na_2SO_3	after 10-15 seconds, the sol-gel piece began to break up into tiny sol-gel pieces; eventually, only small sol-gel pieces remained
Mid-5E	No	2 days	Saturated Na_2SO_3	no cracking observed
Mid-5E	No	2 days	Deionized H_2O	no cracking observed
Mid-6E	No	2 days	Saturated Na_2SO_3	no cracking observed
Mid-6E	No	2 days	Deionized H_2O	extensive cracking observed
Mid-7E	No	2 days	Saturated Na_2SO_3	sol-gel cracked in half
Mid-7E	No	2 days	Deionized H_2O	extensive cracking observed
Mid-8E	No	2 days	Saturated Na_2SO_3	no cracking observed
Mid-8E	No	2 days	Deionized H_2O	no cracking observed
Mid-1M	No	2 days	Saturated Na_2SO_3	sol-gel piece shattered into several (>20) pieces
Mid-2M	No	2 days	Saturated Na_2SO_3	sol-gel piece shattered into several (>20) pieces
Non-1E and Non-2E	No	4 days	95% Ethanol	a few chips (2-3) broke off of the sol-gel piece

Table 3-4: Cracking of Sol-Gels in Aqueous Solution (continued)

Sol-Gel	Triton-X?	Length of Sol-Gel Drying Time	Aqueous Solution	Observations Upon Immersion of the Sol-Gel in the Specified Aqueous Solution
Non-1E	No	4 days	1.00×10^{-4} M MB	sol-gel piece shattered into smaller pieces
Non-3E, 4E, 5E and 6E	Yes (100 µL)	3 days	Deionized Water	no cracking observed
Non-4E	Yes (100 µL)	11 days	1.00×10^{-4} M MB	sol-gel piece shattered into smaller pieces
Non-5E	Yes (100 µL)	11 days	1.00×10^{-5} M MB	sol-gel piece shattered into smaller pieces
Non-6E	Yes (100 µL)	11 days	5.00×10^{-6} M MB	sol-gel piece shattered into smaller pieces
Non-7E	No	4 days	1.00×10^{-5} M MB	sol-gel piece cracked extensively until only tiny sol-gel pieces remained
Non-8E	No	2 days	1.00×10^{-5} M MB	sol-gel piece began to shatter as soon as it was immersed in aqueous MB solution; cracking continued until the sol-gel had broken up into hundreds of tiny sol-gel pieces
Non-10E	No	16 days	1.00×10^{-5} M MB	the cylindrical monolithic sol-gel piece began to crack after approximately 10 seconds in the aqueous MB solution; cracking continued until the sol-gel had broken down into several tiny sol-gel pieces
Non-11E	No	4 days	1.00×10^{-5} M MB	sol-gel piece cracked extensively

Table 3-4: Cracking of Sol-Gels in Aqueous Solution (continued)

Sol-Gel	Triton-X?	Length of Sol-Gel Drying Time	Aqueous Solution	Observations Upon Immersion of the Sol-Gel in the Specified Aqueous Solution
Monolith-6E	No	126 days	1.00×10^{-5} M MB	cracking of monolith began almost immediately upon immersion in the aqueous MB solution and continued until the monolith had shattered into hundreds of tiny sol-gel pieces
Half #1 of Monolith-7E	No	166 days	1.00×10^{-5} M MB	monolith cracked into several tiny pieces
Half #2 Monolith-7E	No	166 days	Deionized H_2O	monolith cracked into several tiny pieces

6. SOL-GELS IN ACIDIC SOLUTION

Post-2M, 3M, 4M and 5M sol-gel pieces were added to solutions of pH 3.0 phosphate buffer (0.1 M) 1 day after they were post-doped. After the sol-gels had been soaked in their respective acidic solutions for 3 days, these solutions appeared light blue in color. Each of the solutions was tested using a Hewlett Packard 8452A Diode Array Spectrophotometer. Deionized water was employed as a blank. A peak in the 600 to 700 nm region was observed for each solution. Since MB absorbs maximally at approximately 661 nm, it appears that MB leached out of these post-doped TMOS sol-gels in acidic solution.

Post-12E sol-gel pieces were added to a solution of pH 3.0 phosphate buffer (0.1 M) 20 days after they were post-doped. After the Post-12E sol-gel pieces had been soaked in the pH 3.0 phosphate buffer for 2 days, the acidic solution still appeared colorless. A similar observation was made for Mid-6E sol-gel pieces 95 days after their preparation.

7. MB-DOPED SOL-GELS IN NA_2SO_3 AND REGENERATION WITH H_2O_2

As explained in the Introduction, MB is a well known redox indicator. In the presence of SO_3^{2-}, MB is reduced to the colorless leuco-MB form. The SO_3^{2-} anion is oxidized to SO_4^{2-} during this process. The blue MB form can be regenerated using H_2O_2 as an oxidizing agent.

Several of the MB-doped sol-gels prepared were added to aqueous Na_2SO_3 solution. Later, many of the sol-gels that had been placed in Na_2SO_3 solution were soaked in H_2O_2 solution. The changes in the colors of these sol-gels in the Na_2SO_3 and H_2O_2 solutions were observed over time and are recorded in Table 3-5.

Table 3-5: MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Mid-1E	1 day	blue	colorless after soaking in saturated SO_3^{2-} solution overnight	sol-gel regained much of its original blue color after soaking in 3% H_2O_2 overnight	colorless after ≅30 minutes of soaking in saturated SO_3^{2-} solution	only very slightly blue after soaking in 3% H_2O_2 solution overnight
Mid-1E	2 days	blue	colorless after ≅32 minutes of soaking in saturated SO_3^{2-} solution			
Mid-1E	3 days	blue	colorless after ≅29 minutes of soaking in saturated SO_3^{2-} solution	a distinct blue color was observed in the sol-gel after ≅75 minutes of soaking in 3% H_2O_2 solution		
Mid-1E	3 days	blue	colorless after soaking in 0.1 M SO_3^{2-} solution overnight			
Mid-1E	4 days	blue	colorless after ≅80 minutes of soaking in 0.1 M SO_3^{2-} solution			
Mid-2E	1 day	bright blue	colorless after soaking in saturated SO_3^{2-} solution overnight			
Mid-2E	12 days	bright blue	remained bright blue after 39 minutes of soaking in saturated SO_3^{2-} solution; colorless after soaking in saturated SO_3^{2-} solution overnight	sol-gel piece regained some, but not all, of its original blue color after soaking in saturated SO_3^{2-} solution overnight		

Table 3-5: MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2 (continued)

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Mid-2E	13 days	bright blue	colorless after ≅52 minutes in saturated SO_3^{2-} solution			
Mid-3E	4 days	blue	colorless after ≅21 minutes in saturated SO_3^{2-} solution	sol-gels appear approximately as blue in color as they had been originally after soaking in 3% H_2O_2 solution overnight	colorless after ≅17 minutes in saturated SO_3^{2-} solution	colorless after soaking in 3% H_2O_2 solution overnight
Mid-3E	11 days	blue	still blue after 63 minutes in saturated SO_3^{2-} solution; colorless after soaking overnight in saturated SO_3^{2-} solution	a very small amount of the sol-gel's original blue color returned after soaking overnight in 3% H_2O_2		
Mid-3E	12 days	blue	still blue after 97 minutes in saturated SO_3^{2-} solution; colorless after soaking overnight in saturated SO_3^{2-} solution			
Post-1E	16 days	dark blue	no color change observed after soaking overnight in saturated SO_3^{2-} solution; sol-gels noticeably lighter in color after 2 days in the SO_3^{2-} solution; after 8 days in the SO_3^{2-} solution, sol-gels even lighter in color but still retain some of blue color	sol-gel pieces appear to have regained some, but not all, of their original blue color after soaking for 6 days in 3% H_2O_2 solution		

Table 3-5: MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2 (continued)

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Post-1E	115 days	dark blue	aqua blue in color (lighter than initial blue color) after ≅18 minutes in saturated SO_3^{2-} solution; parts of the sol-gel were colorless and parts were aqua after soaking overnight in saturated SO_3^{2-} solution	no change in color after 3 days in 30% H_2O_2		
Post-2E	8 days	very light blue	colorless after ≅4 minutes in saturated SO_3^{2-} solution	a slight blue tint returned to the sol-gel after ≅22 minutes in 3% H_2O_2		
Post-3E	5 days	dark blue	original blue color of the sol-gel appeared to have faded significantly but the sol-gel still retained a distinct blue tint after soaking for 6 days in saturated SO_3^{2-} solution			
Mid-1M	3 days	light blue	colorless after soaking in saturated SO_3^{2-} solution	colorless after soaking in 30% H_2O_2 solution overnight		
Mid-1M	6 days	light blue	colorless after soaking in saturated SO_3^{2-} solution	colorless after soaking in 30% H_2O_2 solution for 3 days		
Post-1M	1 day	bright blue	bright blue after soaking in saturated SO_3^{2-} solution for 7 days			

Table 3-5: MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2 (continued)

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Post-4E	84 days	dark blue-purple	dark blue-purple after 5 hours and 20 minutes in saturated SO_3^{2-} solution; aqua-blue in color after soaking overnight in saturated SO_3^{2-} solution	aqua-blue (no change in color) after 3 days in 30% H_2O_2		
Post-5E	84 days	dark purple	light blue-purple in color after soaking for 18 minutes in saturated SO_3^{2-} solution; nearly colorless with a slight blue tint after soaking overnight in saturated SO_3^{2-} solution	colorless with slight blue tint (no change in color) after 3 days in 30% H_2O_2		
Post-6E	84 days	light purple	nearly colorless with slight purple tint after 18 minutes in saturated SO_3^{2-} solution; nearly colorless with slight purple tint after soaking overnight in saturated SO_3^{2-} solution	nearly colorless with slight purple tint (no change in color) after 3 days in 30% H_2O_2		
Mid-4E	4 days	blue-aqua	no change in color after 26 minutes in saturated SO_3^{2-} solution; clear and colorless after soaking overnight in saturated SO_3^{2-} solution	clear and colorless after soaking in 30% H_2O_2 solution for 6 days		

Table 3-5: MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2 (continued)

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Post-7E	35 days	light blue	nearly colorless with a slight blue tint after ≅32 minutes in saturated SO_3^{2-} solution; colorless after soaking overnight in saturated SO_3^{2-} solution			
Mid-5E	2 days	blue	nearly colorless after 58 minutes in saturated SO_3^{2-} solution; colorless after soaking in saturated SO_3^{2-} solution overnight	regained a very slight blue tint (still essentially colorless) after 30 minutes of soaking in 30% H_2O_2 solution; no further change in color after soaking in 30% H_2O_2 solution for 3 days		
Mid-6E	2 days	blue	nearly colorless after 58 minutes in saturated SO_3^{2-} solution; colorless after soaking in saturated SO_3^{2-} solution overnight	a significant amount of the original blue color returned almost immediately upon immersion in 30% H_2O_2 solution (still much less blue than original color); no further change in color after soaking in 30% H_2O_2 solution for 3 days	distinctly blue in color after ≅60 minutes in saturated SO_3^{2-} solution; near colorless with a slight blue tint after ≅90 minutes in saturated SO_3^{2-} solution; colorless after soaking overnight in saturated SO_3^{2-} solution	

Table 3-5: MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2 (continued)

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Mid-7E	2 days	blue	nearly colorless after 58 minutes in saturated SO_3^{2-} solution; colorless after soaking in saturated SO_3^{2-} solution overnight	a significant amount of the original blue color returned almost immediately upon immersion in 30% H_2O_2 solution (still much less blue than original color); no further change in color after soaking in 30% H_2O_2 solution for 3 days	distinctly blue in color after ≅60 minutes in saturated SO_3^{2-} solution; near colorless with a slight blue tint after ≅90 minutes in saturated SO_3^{2-} solution; colorless after soaking overnight in saturated SO_3^{2-} solution	
Mid-8E	2 days	blue	nearly colorless after 58 minutes in saturated SO_3^{2-} solution; colorless after soaking in saturated SO_3^{2-} solution overnight	regained a very slight blue tint (still essentially colorless) after 30 minutes of soaking in 30% H_2O_2 solution; no further change in color after soaking in 30% H_2O_2 solution for 3 days		
Post-10E	13 days	dark blue-aqua	blue-aqua (much lighter than original color) after 32 minutes in saturated SO_3^{2-} solution; light aqua after soaking overnight in saturated SO_3^{2-} solution			
Post-8E	13 days	dark aqua-blue	dark aqua-blue (no change in color) after 18 minutes in saturated SO_3^{2-} solution; very light aqua in color after soaking overnight in saturated SO_3^{2-} solution	regained some of original blue color after soaking for 35 minutes in 30% H_2O_2	sol-gels lost much of blue color after 45 minutes in saturated SO_3^{2-} solution	no change in color after soaking for 3 days in 30% H_2O_2

Table 3-5. MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2 (continued)

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Post-8E	40 days	dark aqua-blue	aqua in color (much lighter than original blue color) after 28 minutes in saturated SO_3^{2-} solution; light aqua in color after 66 minutes in saturated SO_3^{2-} solution; near colorless with a slight aqua tint after 4 days in saturated SO_3^{2-} solution	distinctly aqua in color but not as bright as original color after 35 minutes in 30% H_2O_2		
Post-11E	4 days	blue	blue (no change in color) after 18 minutes in saturated SO_3^{2-} solution; very light aqua in color after soaking overnight in saturated SO_3^{2-} solution	no change in color after 3 days in 30% H_2O_2		
Post-2M	20 days	dark blue	dark blue after 15 minutes in saturated SO_3^{2-} solution; nearly colorless with a slight blue tint after 4 days in saturated SO_3^{2-} solution	no color change after 60 minutes in 30% H_2O_2		
Post-2M	26 days	dark blue	dark blue after 82 minutes in saturated SO_3^{2-} solution; bright aqua (less blue that initial color) after 5 days in saturated SO_3^{2-} solution	no color change after soaking overnight in 30% H_2O_2		
Post-3M	20 days	dark blue	dark blue after 15 minutes in saturated SO_3^{2-} solution; distinctly blue in color but lighter than initial blue color after 4 days in saturated SO_3^{2-} solution	no color change after 60 minutes in 30% H_2O_2		

Table 3-5: MB-Doped Sol-Gels in Na_2SO_3 and H_2O_2 (continued)

Sol-Gel	Drying Time	Initial Color	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution	Color After Soaking in SO_3^{2-} Solution	Color After Soaking in H_2O_2 Solution
Post-3M	26 days	dark blue	dark blue after 82 minutes in saturated SO_3^{2-} solution; light aqua in color after 5 days in saturated SO_3^{2-} solution	no color change after soaking overnight in 30% H_2O_2		
Post-4M	20 days	dark blue	dark blue after 15 minutes in saturated SO_3^{2-} solution; distinctly blue in color but lighter than initial blue color after 4 days in saturated SO_3^{2-} solution	no color change after 60 minutes in 30% H_2O_2		
Post-4M	26 days	dark blue	dark blue after 82 minutes in saturated SO_3^{2-} solution; some sol-gel pieces appeared colorless while others were slightly aqua in color after 5 days in saturated SO_3^{2-} solution	no color change after soaking overnight in 30% H_2O_2		
Post-5M	20 days	dark blue	dark blue after 15 minutes in saturated SO_3^{2-} solution; distinctly blue in color but lighter than initial blue color after 4 days in saturated SO_3^{2-} solution	no color change after 60 minutes in 30% H_2O_2		
Post-5M	26 days	dark blue	dark blue after 82 minutes in saturated SO_3^{2-} solution; light aqua after 5 days in saturated SO_3^{2-} solution	a small amount of MB appeared to have been regenerated within the sol-gels after 35 minutes in 30% H_2O_2; no further color change observed after soaking overnight in 30% H_2O_2		

8. REGENERATION STUDIES WITH NO_3^-, IO_3^- AND $CR_2O_7^{2-}$

Mid-1E, 2E and 3E sol-gels were soaked in saturated SO_3^{2-} solution for 214, 367 and 281 minutes, respectively. Afterwards, all of the sol-gels appeared clear and colorless. These sol-gels were then used to perform regeneration studies using NO_3^-, IO_3^- and $Cr_2O_7^{2-}$, respectively.

A. NO_3^-: Some Mid-2E colorless sol-gel pieces were added to a solution of 0.1 M KNO_3. After soaking in the NO_3^- solution for 6 days, the sol-gel pieces still appeared clear and colorless. Similar observations were made using the colorless Mid-1E and Mid-3E sol-gels.

B. IO_3^-: Some Mid-2E colorless sol-gel pieces were added to a solution of 0.1 M KIO_3. No blue color returned to these sol-gels after 5 days of soaking in the IO_3^- solution.

Some Mid-3E colorless sol-gel pieces were also added to a solution of 0.1 M KIO_3. The sol-gel pieces had a distinct blue tint after being soaked in the IO_3^- solution for 1 day. After having been soaked in the IO_3^- solution for 3 days, the sol-gel pieces appeared to have regained much, if not all, of their original blue color. These sol-gel pieces were then added to a solution of saturated SO_3^{2-}. Overnight, the sol-gel pieces turned from blue to colorless. The original blue color of the sol-gels did not return after they were soaked in 0.1 M IO_3^- solution a second time. Similar observations were made for the Mid-1E sol-gel pieces.

C. $Cr_2O_7^{2-}$: Some Mid-2E sol-gel pieces were added to an orange solution of 0.1 M $K_2Cr_2O_7$. A blue tint was visible in these sol-gel pieces after approximately 45 minutes of soaking. When taken out of the $Cr_2O_7^{2-}$ solution and rinsed with deionized water, however, these sol-gel pieces appeared yellow in color. After soaking for 87 minutes, the sol-gels appeared greenish in color when taken out of the $Cr_2O_7^{2-}$ solution. The color of

these sol-gels did not change after they had been soaked for 1 day in the $Cr_2O_7^{2-}$ solution. The sol-gels were transferred to a solution of saturated SO_3^{2-} and remained green in color after 1 day of soaking in this solution. The sol-gels were removed from the SO_3^{2-} solution and soaked in deionized water for 2 days. They were then transferred to another solution of saturated SO_3^{2-}. The sol-gel pieces still appeared green in color after 1 day of soaking in the SO_3^{2-} solution. Similar observations were made for the Mid-1E and Mid-3E sol-gel pieces.

9. SOL-GELS IN AIR

The Mid-3E sol-gel pieces were originally a distinct blue color. When viewed 146 days after their preparation, however, the sol-gels appeared clear and colorless. A similar observation was made for the Post-2E sol-gel pieces. These pieces were a distinct blue color, although very light when first prepared. The same sol-gel pieces appeared completely clear and colorless 146 days after they were post-doped.

Other sol-gels changed from blue to purple in air. For example, the Post-5E sol-gel pieces converted from bright blue to purple in color. Similarly, the Post-6E sol-gels converted from bright blue in color to lavender. These observations were made 79 days after the Post-5E and Post-6E sol-gel pieces were post-doped.

10. SOL-GEL COATED GLASS SLIDES

The white-water glass slides that were washed with either acid and base (Table 2-6) or with methanol (Table 2-7) before being coated with sol-gel were observed. As drying of the sol-gel coatings proceeded, the coatings peeled off of the white-water glass slides.

Extensive peeling was observed for all of the white-water glass slides that were coated with sol-gel.

Glass borosilicate slides 5MeOH through 9MeOH were coated using the same TEOS sol-gel batch. After the sol-gel coatings on these slides had been allowed to dry, the sol-gel coatings on the slides that were dip coated earliest (5MeOH to 7MeOH) were observed to be flaking off of the slides. Also, light was reflected and refracted from the sol-gel coatings on these slides. The slides that were dip coated in sol-gel later on (8MeOH and 9MeOH) were more evenly coated. In fact, the last slide to be dip coated, 9MeOH, did not have any apparent flakes in its sol-gel coating.

Slide-9MeOH was added to a petri dish that contained MB solution ($\cong 10^{-4}$ M) in an attempt to post-dope its sol-gel coating. Although a few tiny sol-gel flakes were seen floating in the aqueous MB solution after Slide-9MeOH had been soaked for a few minutes, the majority of the sol-gel coating remained attached to the slide during the soaking process. After approximately 4 hours of soaking in the MB solution, it appeared that the sol-gel coating had taken up some MB. The sol-gel coated slide was removed from the MB solution and soaked in deionized water for approximately 5 minutes. The sol-gel coated slide appeared distinctly blue in color after this soaking period. It appears, then, that the sol-gel coating on the slide was post-doped. Slide-9MeOH was allowed to dry at room temperature. An absorption spectrum of Slide-9MeOH was taken using a Hewlett Packard 8452A Diode Array Spectrophotometer and the non-doped, sol-gel coated Slide-8MeOH as a blank. This spectrum is labeled as Figure 3-1. There is a significant peak in the blue region of the spectrum (600 to 700 nm) indicating the presence of MB in the sol-gel coating.

Slide-9MeOH was then added to saturated SO_3^{2-} solution. After soaking overnight in this solution, the slide appeared clear and colorless. The sol-gel was still evenly coated over the slide but the blue color within the sol-gel coating was no longer present. An absorption spectrum of Slide-9MeOH was taken using a Hewlett Packard 8452A Diode

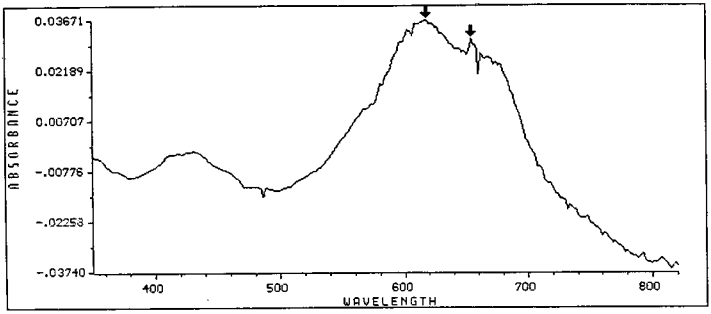


Figure 3-1: Absorption spectrum of MB post-doped Slide-9MeOH.

Spectrum taken with a Hewlett Packard 8452A Diode Array Spectrophotometer.

Non-doped, sol-gel coated Slide-8MeOH used as a blank.

Array Spectrophotometer and the non-doped, sol-gel coated Slide-8MeOH as a blank. This spectrum is displayed in Figure 3-2. The peak observed in the 600 to 700 nm region that was observed in Figure 3-1 is no longer present in Figure 3-2 indicating that MB is no longer present in the sol-gel coating. Slide-9E was then added to a solution of 30% H_2O_2 in an attempt to regenerate the MB within the sol-gel coating. After 2 days in the H_2O_2 solution, there was still an even sol-gel coating on Slide-9E and the slide appeared clear and colorless. The slide was removed from the H_2O_2 solution, rinsed thoroughly with deionized water and allowed to dry at room temperature. An absorption spectrum of this slide was again taken using a Hewlett Packard 8452A Diode Array Spectrophotometer and the non-doped, sol-gel coated Slide-8MeOH as a blank. No significant peak was observed in the 600 to 700 nm region indicating that MB was not regenerated within the sol-gel coating of the microscope slide (Figure 3-3).

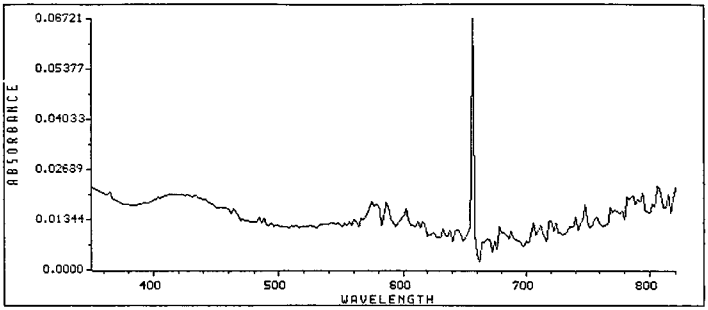


Figure 3-2: Absorption spectrum of MB post-doped Slide-9MeOH after soaking in SO_3^{2-} solution.

Spectrum taken with a Hewlett Packard 8452A Diode Array Spectrophotometer.

Non-doped, sol-gel coated Slide-8MeOH used as a blank.

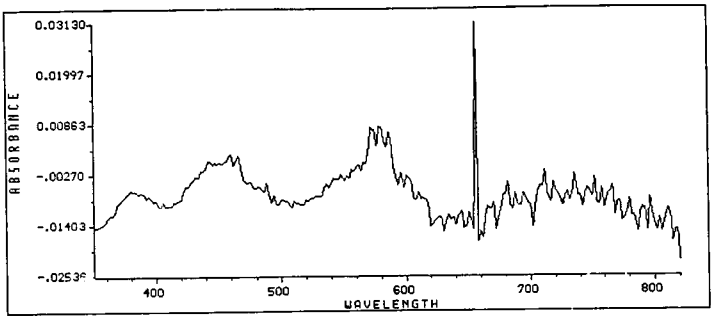


Figure 3-3: Absorption spectrum of MB post-doped Slide-9MeOH after soaking in H_2O_2 solution.

Spectrum taken with a Hewlett Packard 8452A Diode Array Spectrophotometer.

Non-doped, sol-gel coated Slide-8MeOH used as a blank.

CHAPTER 4

DISCUSSION AND FUTURE WORK

1. CONVERSION OF MB TO LEUCO-MB WITHIN THE PREPARED SOL-GELS

A. Sol-Gels in Deionized Water: From Table 3-3 it can be seen that the majority of MB-doped sol-gels soaked in deionized water for an extended period of time changed from blue in color to colorless. There are three possible explanations for this phenomenon. First, the MB could be leaching out of the sol-gels in the MB form. Second, the MB could be leaching out of the sol-gels in the colorless leuco-MB form. A third possible explanation is that the MB could be converting to the leuco-MB form within the sol-gels.

If the MB was leaching out of the sol-gels in the MB form, one would expect to see the water samples in which the sol-gels were soaked turn blue as they became increasingly concentrated in MB. As described in Chapter 3, 3B, MB was not detected in any of the deionized water samples in which MB-doped sol-gels were soaked. It does not appear, then, that MB is leaching out of the sol-gels in the MB form.

Recall that colorless leuco-MB is converted to the blue MB form in the presence of O_2 (Introduction). Because O_2 was present in the deionized water samples in which the MB-doped sol-gels were soaked, one would expect any leuco-MB in these water samples to be converted gradually to MB. If the MB was leaching out of the sol-gels in the leuco-MB form, then, one would expect the blue color of MB to be generated in the deionized water samples over time. As described in Chapter 3, 3B, absorbance due to MB was not detected in any of the deionized water samples in which MB-doped sol-gels were soaked. It does not appear, then, that the MB is leaching out of the sol-gel in the leuco-MB form.

Since the first two explanations for the loss of color in the MB-doped sol-gels in deionized water have been discredited, it is probable that the third explanation is the correct one. In other words, it appears that the MB within the MB-doped sol-gels is converting to the leuco-MB. No leaching of the MB from the sol-gel matrices appears to be occurring.

B. Sol-Gels in Air: As described in Chapter 3, 9, the Mid-3E and Post-2E sol-gels changed from blue in color to colorless in air. Since there is no possibility that MB leached out of these sol-gels and into solution, it appears that the MB was converted to the leuco-MB form within these sol-gels.

C. Regeneration of MB within Sol-Gels: From the data in Table 3-5, it is apparent that all of the MB-doped sol-gels studied became lighter in color after soaking in SO_3^{2-} solution with the exception of the Post-1M sol-gel pieces. Since MB does not appear to be leaching out of the sol-gels (Chapter 4, 1A), it appears that the SO_3^{2-} anions are diffusing into the sol-gels and causing the conversion of MB to leuco-MB within these sol-gels. This conversion takes place consistently and typically within 2 hours of the addition of an MB-doped sol-gel to SO_3^{2-} solution (Table 3-5).

The regeneration of MB from the leuco-MB within the sol-gels has not been as successful. MB has not been fully regenerated within the sol-gels more than once in any of the sol-gels studied when H_2O_2 (Table 3-5), NO_3^-, IO_3^- or $Cr_2O_7^{2-}$ (Chapter 3, 8) was used as the oxidant and was not regenerated at all in several of the sol-gels studied. The difficulty in regenerating MB from the leuco-MB within the sol-gels again suggests that MB prefers to exist in the leuco-MB form within the TMOS and TEOS sol-gels.

D. Possible Explanations: As suggested in 1A, 1B and 1C, above, it appears that MB prefers to exist in the leuco-MB form in the TMOS and TEOS sol-gels that were prepared.

From Figure 1-2, it can be seen that leuco-MB has two nitrogen-hydrogen bonds in its structure. The hydrogen atoms in these bonds are capable of hydrogen bond donation. MB does not contain any hydrogen atoms which can participate in hydrogen bonding. The leuco-MB form, then, is more able to form hydrogen bonds with the oxygen atoms in a

TMOS or TEOS sol-gel network than is MB. This could be one reason why MB prefers to exist in the leuco-MB form within the prepared sol-gels.

Flavin molecules, which often function as cofactors in protein molecules, are similar in structure to MB. In a crystallization study performed on flavins, the oxidized flavin molecules were found to be relatively flat whereas the reduced flavin molecules were shown to be slightly bent [12]. If MB also exhibits this change in shape, with the oxidized MB existing as a relatively flat molecule and the reduced leuco-MB existing in a slightly bent form, it could provide another explanation for the preference of leuco-MB over MB within the sol-gels. This structural change is consistent with the observed spectral properties of MB. When MB is reduced, it is converted from the red-absorbing blue form to the colorless leuco-MB form. For this color change to occur, there must be a significant loss in the conjugation of MB when it is reduced to leuco-MB. If leuco-MB exists in a bent conformation, this would account for the large loss of conjugation in this molecule. Moreover, if the pore sizes within the sol-gels are small, the slightly bent leuco-MB may fit better within the pores of the sol-gel network than the relatively flat MB, causing the leuco-MB form to be more favorable within the sol-gels.

Future work may focus on preparing MB-doped sol-gels with larger pore sizes. This could be done by using larger alkoxide precursors to prepare the pre-sol-gel mixtures. With larger pore sizes, the effect of leuco-MB possibly having a structure that fits more easily in the sol-gel pores than MB would be diminished.

For MB to be converted to the leuco-MB form within the sol-gels, a reducing agent must be present. This reducing agent is, at present, unknown. It is possible that the two factors mentioned above - the ability of leuco-MB to hydrogen bond to the sol-gel network more strongly than MB and the pore size of the sol-gel network - could be driving this reduction. Future work will focus on identifying the reducing agent in the MB-doped TMOS and TEOS sol-gel systems.

2. CONVERSION OF MB TO A PURPLE SPECIES WITHIN SOL-GELS

Several MB-doped sol-gels, including Mid-3E, Mid-6E, Mid-7E, Mid-8E, Post-1E, Post-5E, Post-6E, Post-7E and Post-8E, converted from blue in color to purple or purple-blue when soaked in deionized water (Table 3-3). The Post-5E and Post-6E sol-gels were converted from blue to purple and lavender, respectively, in air (Chapter 3, 9).

The purple species that formed within these sol-gels is unknown. Future studies may be directed towards determining the spectral properties of this purple species. Borosilicate glass slides could be coated with MB-doped sol-gel via the procedure described in Chapter 2, 4 and Chapter 3, 10. The slides could be stored either in air or in deionized water and the absorbance spectra of the MB-doped sol-gel coatings could be monitored over time.

3. CRACKING OF SOL-GELS IN AQUEOUS SOLUTION

Some pieces from the Mid-3E (4-day dried), Mid-4E (4-day dried), Mid-5E (2-day dried) and Mid-8E (2-day dried) sol-gel batches were added to deionized water while other pieces from these batches were added to saturated Na_2SO_3 solution. For each of these sol-gel types, the observations made for the sol-gel pieces placed in water were the same as those observations made for the sol-gel pieces immersed in saturated Na_2SO_3 solution (Table 3-4). Similarly, when one half of Monolith-6E (166-day dried) was added to deionized water solution and the other half was soaked in 1.00×10^{-5} M MB solution, both monolith halves cracked into several tiny pieces (Table 3-1). There were cases, however, in which sol-gels from the same batch exhibited different cracking behavior in aqueous solutions that contained different solutes. For example, sol-gel pieces from the Mid-6E (2-day dried) and Mid-7E (2-day dried) batches each exhibited different behavior in deionized water than they did in saturated Na_2SO_3 solution (Table 3-4). The effect that

different solutes have on the cracking behavior of sol-gels in aqueous solution is unclear from these results.

The effect of increased sol-gel drying time on the extent of cracking in aqueous solution is also indeterminate from the data listed in Table 3-4. Sol-gel pieces from the Mid-3E sol-gel batch were placed in saturated Na_2SO_3 solution after 4 days of drying, whereas other sol-gel pieces from the same batch were added to saturated Na_2SO_3 solution after 12 days of drying. The Mid-3E sol-gel piece that was dried for 4 days shattered in aqueous solution; the Mid-3E sol-gel piece placed in aqueous solution after 12 days of drying only had a few (2-3) chips break off of it (Table 3-4). It appears from these results, then, that the tendency for sol-gels to crack in aqueous solution decreased with increased drying time; however, the results obtained for Monoliths-6E and 7E are not consistent with this, however. These Monoliths, dried for relatively long periods of time (126 days and 166 days, respectively), both shattered upon immersion in aqueous solution. Also, sol-gels Mid-5E, Mid-6E and Mid-8E did not crack in aqueous Na_2SO_3 solution after only 2 days of drying. A strong correlation between the length of sol-gel drying time and the extent of sol-gel cracking in aqueous solution, then, was not found for the sol-gels prepared in this study.

According to the literature [5], cracking of sol-gels upon immersion in aqueous solution is a result of stress in the sol-gels that is created during the drying process. It is proposed that when the sol-gels dry, some of the larger pores are emptied while some of the smaller pores retain solvent. This creates large internal pressure gradients within the sol-gels which cause the sol-gels to crack in aqueous solution.

Triton-X was added during the preparation of the "sol" for several of the sol-gels prepared (Chapter 2, 2A). It has been suggested that the addition of Triton-X to sol-gels during the preparation procedure could decrease the extent of the cracking of sol-gels in aqueous solution [5]. Some sol-gels prepared with Triton-X, including Mid-2E (14-day dried) and Non-3E through Non-6E (3-day dried), did not crack in aqueous solution.

Others, including Mid-2E (1-day dried), Mid-3E (4-day dried), Mid-3E (12-day dried) and Non-4E through Non-6E (11-day dried), cracked extensively. Triton-X did not have any clear effect on the cracking behavior of the sol-gels prepared in this study.

4. SOL-GELS IN BASIC SOLUTION

Some Mid-1E sol-gels (2-day dried) dissolved after soaking overnight in 6 M NaOH solution while some Post-2M sol-gels (61-day dried) did not dissolve after 2 days in 6 M NaOH solution. Future work could focus on determining whether TMOS sol-gels are more resistant to hydrolysis in basic solution than TEOS sol-gels and on determining whether increased sol-gel drying time causes an increase in the resistance of silica-based sol-gels to basic solution.

5. SOL-GELS IN ACIDIC SOLUTION

MB leached out of the Post-2M, 3M, 4M and 5M sol-gel pieces when these pieces were soaked in pH 3.0 phosphate buffer (0.1 M) 1-day after post-doping. No leaching was observed from the Post-12E sol-gel pieces (20 days after post-doping) or from the Mid-6E sol-gel pieces (95-day dried) in pH 3.0 phosphate buffer (0.1 M).

Future experiments could focus on determining whether MB leaches more easily from TMOS sol-gels than from TEOS sol-gels in acidic solution. Other experiments could be performed to determine whether leaching of MB from post-doped sol-gels in acidic solution decreases as the number of days since post-doping increases.

6. CONCLUSION

MB-doped sol-gels suitable for use as disposable SO_3^{2-} sensors have been prepared. Since regeneration of MB within these sol-gels has been a problem, however, a reversible sol-gel SO_3^{2-} sensor has not been made successfully. Future work should focus on improving the regeneration of MB within the sol-gels and on determining why MB prefers to exist in the leuco-MB form or in a purple form within the sol-gels.

Once these obstacles have been overcome, experimentation should be directed towards coating optical fibers with MB-doped sol-gel thin films. These coated fibers could then be connected to an optical excitation source and an optical detector, thereby creating a reversible, MB-doped sol-gel sensor.

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