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Investigating the sensitivity of PMMA optical fibres for use as an evanescent field absorption sensor in aqueous solutions

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Abstract. Polymethylmethacrylate (PMMA) optical fibres are low-cost polymer fibres that are generally more physically robust than silica fibres, are more flexible, yet like silica fibres have the potential to be used for practical evanescent field absorption sensors in aqueous solutions. However, evanescent field absorption in aqueous solutions is influenced by more than just the specific absorptivity of the solution in question. The physical configuration of the optical fibre itself, as well as surface charge interactions between the fibre and the chromophore in the solution also significantly affects the sensitivity of the fibre to evanescent field absorption. This paper reports on an investigation of numerous physical phenomena that influence evanescent field absorption for PMMA fibres using an aqueous solution of the dye Amido-black. Parameters investigated included fibre coiling configuration and bend radius, fibre interaction length, and effect of solution pH. Coiled fibres were found to be more sensitive to evanescent field absorption than straight (uncoiled) lengths, and sensitivity was found to increase with a further reduction in bend radius. At high solution pH, the absorption versus solution concentration proved to be linear whereas at low pH the absorption versus concentration relationship exhibited a clear deviation from linearity. The observed non-linearity at low pH points to the importance of accounting for electrostatic interactions between chromophore and fibre surface when designing a PMMA sensor for evanescent field absorption measurements in aqueous solutions.

1. Introduction

The use of optical fibres in the development of chemical sensors is receiving considerable interest due to numerous advantages of this approach over traditional sensing methodologies. Optical fibres are typically very small in diameter (~10 μm –1 mm), the materials which are often silica or polymers can be chemically and/or biologically inert and intrinsic sensors rely on modification of an optical signal hence are impervious to electromagnetic interference. Optical fibres are generally cylindrical and consist of a central core material, commonly fused silica or plastic, which is surrounded by a

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concentric cladding. The core material has a higher refractive index than the cladding. The cladding is often enclosed in another concentric, plastic, protective jacket which protects the cladding and increases the flexibility of the fibre. Radiation introduced into the core at one end of an optical fibre travels down the core via numerous total-internal reflections at the core-cladding interface. Optical interference occurs between parallel wavefronts during the succession of skips along the fibre core and solution of Maxwell's equations for the resulting standing waves indicates that some of the radiation, at the core-cladding interface, penetrates some distance into the cladding. This is the *evanescent field*.

The depth of penetration, d_p, is defined as the distance into the cladding over which the evanescent field is reduced to 1/e of its interface-value, and can be calculated using [1]

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2\phi - n_2^2}} \qquad (1)$$

where λ is the wavelength of the light propagating down the fibre, n_1 is the refractive index of the core material, n_2 is the refractive index of the surrounding cladding, and ϕ is the angle of incidence at the core-cladding interface. If the cladding has been removed and the core immersed in a liquid medium of lower refractive index than the core, then liquid behaves as the cladding and the evanescent field penetrates some distance into the liquid. If the liquid itself is optically absorbing at certain wavelengths, hitherto referred to as a *chromophore*, the interaction between the evanescent field and the chromophore involves the process of optical absorption, and results in attenuation of the intensity of the radiation along the fibre. The reduction in intensity may be measured and related to the concentration of the chromophore in contact with the fibre core in the same way as traditional optical absorption measurements. A thorough treatment of evanescent spectroscopy can be found elsewhere [1].

The optical fibre evanescent field absorption (*FEFA*) technique offers numerous advantages over conventional absorption methods that involve the use of cuvettes. Firstly, the net absorbing path length can be considered as the sum of small incremental displacements of the evanescent field at each point of internal reflection at the core-liquid interface [2]. Thus the effective absorbing path-length can be made very small (~μm) and FEFA can therefore be directly applied to strongly absorbing chromophores. In conventional spectroscopic absorption measurements of strongly absorbing chromophores, sample dilution would be required to maintain instrument linearity. However, the FEFA path-length can be duly increased by simply increasing the interaction length of the optical fibre (that is the length of the fibre with an exposed core-liquid interface). Moreover, while sensitive to chromophores, the small evanescent field penetration depths involved have been observed to render FEFA insensitive to the presence of any scattering particles also contained in the chromophore sample [3].

Due to its inherent potential as a spectroscopy tool, numerous researchers have investigated the process of FEFA, especially the role of surface interactions between the chromophore species and the optical fibre core. In one such example, the observed evanescent absorbance of a candidate dye, methylene blue, has been shown to be orders of magnitude greater than that predicted by theory [4]. It was subsequently proposed that the sensitivity of FEFA revolved around the electrostatic interaction between the chromophore and the exposed section of fibre core. A number of other studies have also reported non-linear absorbance *v.* concentration for FEFA data using silica-core fibres [3,5,6]. The higher-than-predicted absorption observed by Ruddy et al [4], and the non-linear nature of absorption versus chromophore concentration observed by others suggests adsorption of the dye molecules onto the polar fibre surface may occur. In the case of a silica-core fibre, the high density of OH-groups at the fibre surface could be expected to influence the actual concentration of polar dye molecules present at the surface.

If this is the case, then the electrostatic shielding length, λ_D, of the chromophore will be of critical importance. This shielding length can be described by a modified Coulomb potential

$$\lambda_D = \sqrt{kT\varepsilon / e^2 n_e} \tag{2}$$

where k is the Boltzmann constant, T is temperature, ε is the permittivity of the medium, e is the charge of an electron and n_e is the ion density [4]. Equation 2 shows that the shielding length is inversely proportional to the square-root of the ion density.

Research conducted to date has focussed on the use of plastic-cladded, silica-core (PCS) fibres. However, one practical limitation of using silica-core fibres is that when a section of cladding is removed, the exposed fibre core is very brittle and this imposes restrictions on sensor design such as limiting interaction length as well as precluding bending of fibres and applications involving moving fluids. One alternative to silica-core optical fibres are polymers such as polymethylmethacrylate (PMMA). PMMA optical fibres are actually comparatively cheaper than silica fibres, and are considerably more flexible when jacketed, unjacketed and when prepared with a section of exposed core.

PMMA comprises the molecular subunit, or monomer, depicted in figure 1. As the oxygen atoms within the PMMA monomer are electronegative, partial negative charge resides on them, whilst the resulting partial positive charge resides on the central carbon atom [7].

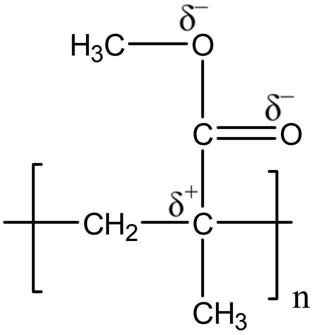


Figure 1. The molecular subunit of PMMA

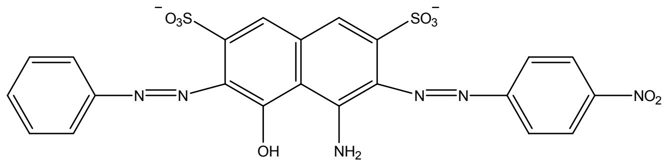
The result of this partial charge separation is that a fibre made from PMMA will have a net negative charge at the surface of the fibre where the oxygen atoms within the PMMA monomer sit.

In this paper, we report on an investigation into some of the key characteristics of PMMA optical fibres relevant to their use as evanescent field sensors. These include the impact on sensitivity of fibre interaction length, bend radius and electrostatic interactions between chromophores and the PMMA core.

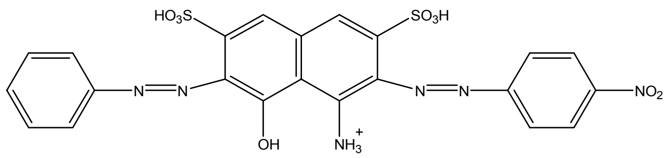
2. Materials and methods

The liquid chromophore used in this current investigation was based on a stock solution of Amido black dye (also known as Naphthol Blue Black purity ~ 80%, Sigma Aldrich, USA) in distilled water. Amido black is a pH sensitive dye insofar as the local pH will influence the degree of protonation of the dye molecule. At low pH (ph $\approx$ 2) the molecule will have a positive charge in solution whereas at high pH (pH $\approx$ 12) the molecule will have a net negative charge. The two forms of the Amido black dye molecule are depicted in figure 2.

Through progressive dilutions with distilled water, dye concentrations of between $1 - 8 \times 10^{-4}$ M were prepared. In order to investigate the influence of fibre surface-chromophore interaction, the pH of the dye solutions was controlled using either sodium hydroxide (NaOH) for high pH or hydrochloric acid (HCl) for low pH.



(i)



(ii)

Figure 2. The deprotonated form, high pH, (i) and the protonated form, low pH, of Amido black in aqueous solution.

A schematic diagram of the FEFA apparatus used in thisinvestigation is given in figure 3. Light from a polarised 4 mW Helium/Neon laser (λ = 633 nm, Uniphase, CA USA) was coupled into a length of PMMA optical fibre (core diameter 250 μm, overall diameter with cladding 265 μm, LG265-48, Regal Lighting Systems, NSW Aust.) using a precision optical coupler (M-F-91TS, Newport, Irvine CA USA).

The fibre cladding was removed by wiping the fibre with a tissue soaked in acetone. The process of wetting and wiping was repeated until a clean, smooth surface was obtained [8]. The prepared lengths of PMMA fibre were inserted into a sample cell, hitherto referred to as the *FEFA Cell*, constructed from Perspex and designed to allow for small sample volumes, ease of cleaning and simple removal or replacement of fibres.

Where fibre coiling was required, unclad sections of the fibre were initially coiled around a cylindrical glass support and fixed in place using adhesive tape.

The attenuated radiation emerging from the downstream end of the PMMA fibre was detected with a photodetector (Industrial Fiber Optics, Model IF-511, AZ USA). In response to the presence of the chromophore solutions, the measured absorbance at 633 nm was calculated from the photodetector readings using

$$Abs_{633} = -\log_{10}\left(\frac{P_{\text{Sample}}}{P_{\text{Reference}}}\right) \tag{3}$$

where P_{Sample} was the power reading when the measurement fibre was immersed in the chromophore solution and $P_{\text{Reference}}$ the power reading when the fibre was immersed in distilled water.

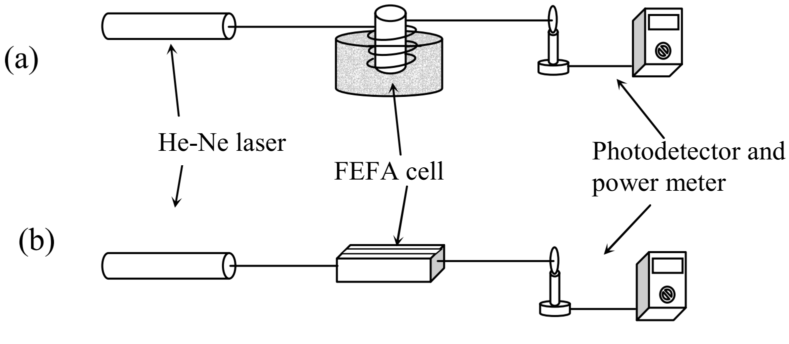


Figure 3. Schematic diagram of the FEFA apparatus for (a) coiled and (b) straight lengths of PMMA fibre.

3. Results and discussion

PMMA absorbance readings as a function of concentration of chromophore are depicted in figure 4. Measurements are shown for two series of dye solution, one series at a pH of 2 and the second at a pH of 12. At a pH of 2 there is a distinct non-linearity in the absorbance versus concentration plot. At a pH of 12, however, the absorbance versus concentration plot is linear, although the absorbance values are significantly lower in magnitude.

As the PMMA-core fibre used in this study is polar with a net negative surface charge, at pH 2 where the chromophore carries a net positive charge, electrostatic interactions will result in some of the dye molecules being attracted to the surface of the fibre and this is characterised by the electrostatic shielding length discussed earlier. Increasing the chromophore concentration will have two consequences; namely electrostatic repulsion will occur between the increasing amounts of positive ions in the bulk liquid and the positive ions in the accumulated space charge sheath surrounding the fibre core; and the electrostatic sheath will shrink around the fibre core according to equation 2. The combined effect is only expected to be relatively small since, according to equations 1 and 2, the electrostatic shielding length occupies only a few percent of the evanescent field penetration depth. Nonetheless, the net result of these interactions is the appreciable deviation from linearity at pH = 2 in figure 4.

When the pH is increased to 12, owing to negative polarity configuration of the dye molecules, the space-charge effects discussed earlier are absent and a predictable Beer-Lambert linearity between absorbance and chromophore concentration now exists. Furthermore, in the absence of the concentrating effect of opposite polarity of the chromophore, the absolute absorbance values are also smaller in magnitude than those that occur at the lower pH values.

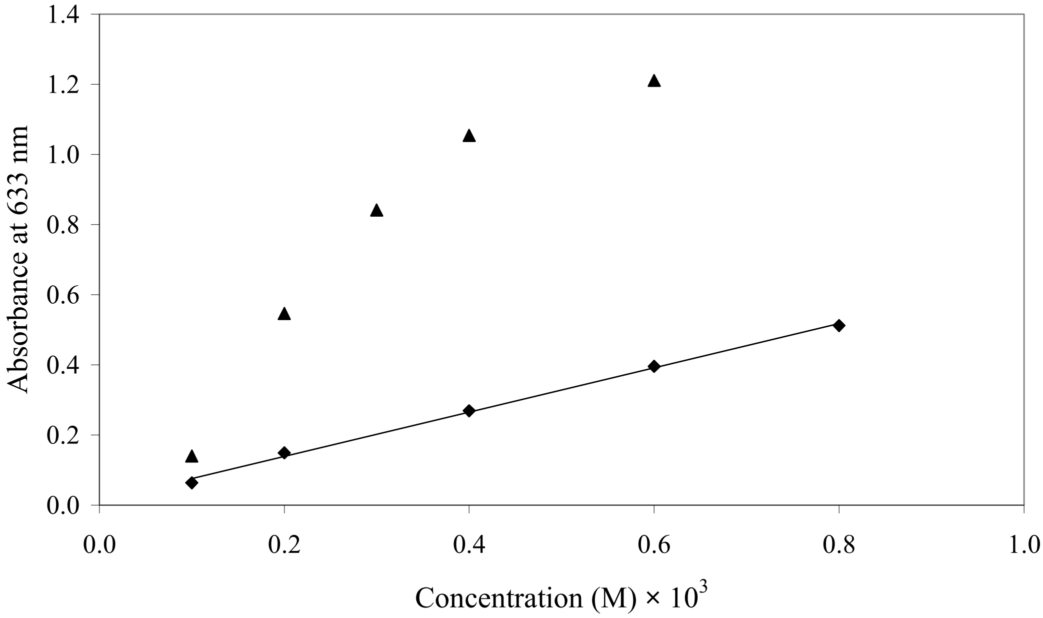


Figure 4. The comparison between the evanescent absorbance *vs* concentration profiles for Amido black solutions at pH 7 (▲) and pH 12(♦).

A plot of the evanescent field absorbance of the PMMA fibre as a function of fibre interaction length is given in figure 5. For a given chromophore concentration the absorbance increases linearly with fibre interaction length. This is due to the simple fact that the net absorption path length is directly linked to the number of skips of the radiation as it propagates along the fibre core, and this is directly proportional to the length of the exposed core. This is a common observation with the FEFA technique [2,4,5].

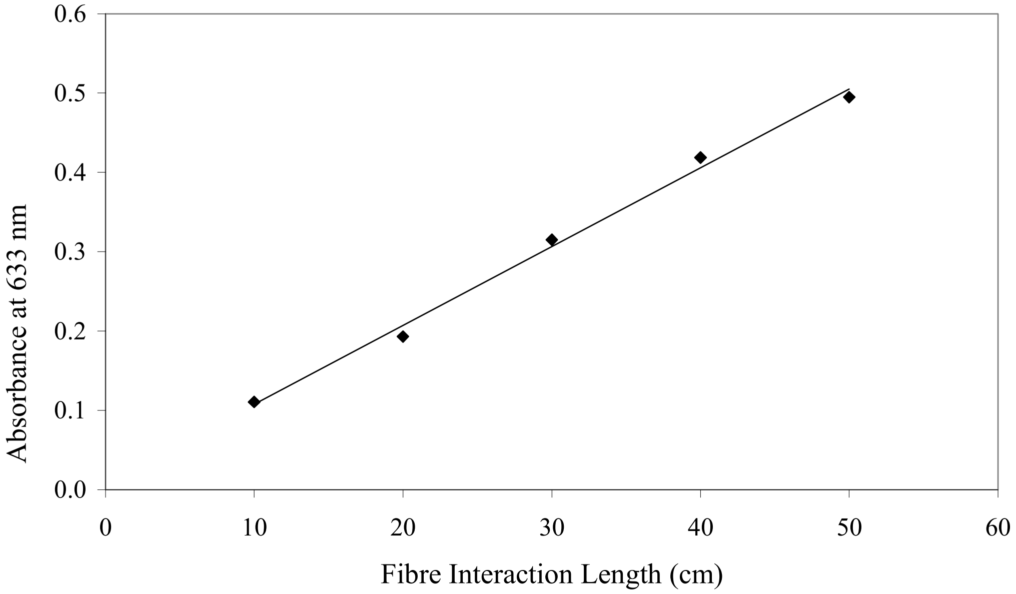


Figure 5. The change in evanescent absorbance with unclad fibre interaction length for a constant dye concentration (2 × 10 $^{-4}$ M at pH 12).

As mentioned earlier, the flexibility of the PMMA fibres facilitates coiling of the unclad section of fibre, something that is not possible with silica fibres. Figure 6 compares the evanescent absorbance for a range of chromophore concentrations resulting from a 10 cm length of unclad PMMA fibre coiled at two different radii as well as that produced from a straight length of the fibre. For any given chromophore concentration, the evanescent absorbance values are higher for the coiled fibres compared to the straight fibre, with the highest sensitivity occurring at the lower coil radius. Reducing the bend radius of the fibre has two consequences on the evanescent field absorbance. Firstly, the average angle of incidence at the core-liquid boundary increases, which, according to equation 1, increases the penetration depth. Secondly, an increase in angle of incidence, increases the number of skips of the propagating radiation along the core-liquid interface per unit fibre length. Both of these result in an increase in the net evanescent field absorption of the radiation. However, one unwanted trade-off associated with this increase in sensitivity is the fact that higher-order modes propagating along the fibre will violate the requirement for total-internal reflection and will be lost into the liquid. This results in a reduction in the net power propagating along the fibre with the attendant decrease in signal-to-noise ratio.

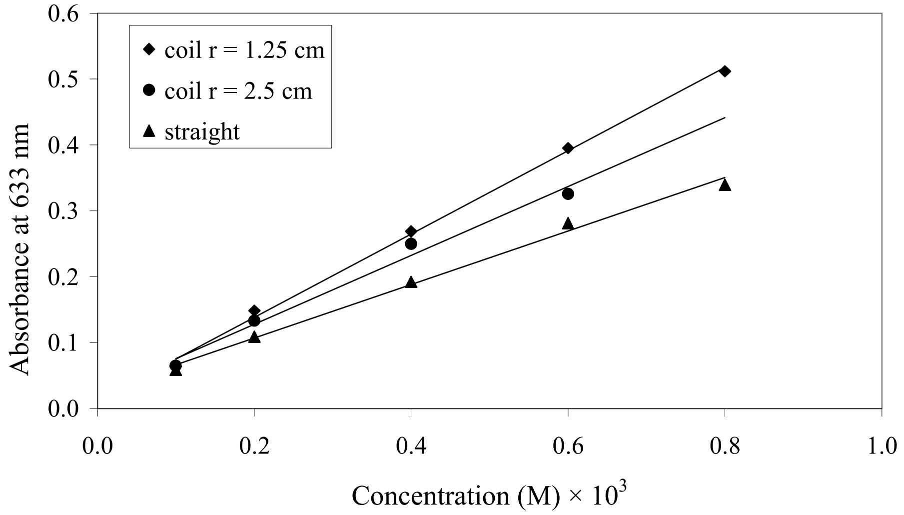


Figure 6. Evanescent absorbance of straight and coiled PMMA fibres, with constant interaction length of 10 cm, using amido black solutions at pH 12. For coiled fibres, *r* is the coil radius.

4. Conclusion

This paper has investigated key characteristics of polymethylmethacrylate optical fibres related to their employment as evanescent field absorption sensors in liquid media. The sensitivity of the fibres to a liquid chromophore is influenced by the polarity of the chromophore owing to electrostatic interactions between the chromophore and the negative surface charge residing on the surface of the fibre core. Furthermore, increasing the length of the exposed core in the liquid, or reducing the bend radius will both result in an increase in sensitivity of the evanescent field absorption measurements with a given concentration of chromophore.

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References

[1] Stewart G 1999 Fiber optic sensors in environmental monitoring In: Optical Fiber Sensing Technology Volume 4: Chemical and Environmental Sensing Eds Grattan K T V and Megitt B T (Kluwer Academic Publishers) 95 - 7.

[2] Lamb D W, Bunganaen Y, Louis J, Woolsey G A, Oliver R L and White G 2004 Fibre evanescent field absorption (FEFA): an optical fibre technique for measuring light absorption in turbid water samples *Marine and Freshwater Research* **55** 533- 43.

[3] Bunganaen Y and Lamb D W 2005 An optical fibre technique for measuring optical absorption by chromophores in the presence of scattering particles. *This journal*

[4] Ruddy V, MacCraith B D and Murphy J A 1990 Evanescent wave absorption spectroscopy using multimode fibres *Journal of Applied Physics* **67** 6070 – 74.

[5] DeGrandpre M D and Burgess L W 1988 Long Path Fiber-Optic Sensor for Evanescent Field Absorbance Measurements *Analytical Chemistry* **60** 2582 – 86.

[6] Deboux B J-C, Lewis E, Scully P J and Edwards R 1995 *Journal of Lightwave Technology* **13** 1407 - 14.

[7] McMurry J 2004 Organic Chemistry 6th Edition (Thomson Brooks/Cole).

[8] Merchant D F, Scully P J and Schmitt N F 1999 Chemical tapering of polymer optical fibre *Sensors and Actuators* **76** 365 – 71.