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Published in:
SENSORS AND ACTUATORS B-CHEMICAL

Document Version:
Peer reviewed version

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Extruded colour-based plastic film for the measurement of dissolved CO₂

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Abstract

Dissolved CO₂ measurements are usually made using a Severinghaus electrode, which is bulky and can suffer from electrical interference. In contrast, optical sensors for gaseous CO₂, whilst not suffering these problems, are mainly used for making gaseous (not dissolved) CO₂ measurements, due to dye leaching and protonation, especially at high ionic strengths (> 0.01M) and acidity (< pH 4). This is usually prevented by coating the sensor with a gas-permeable, but ion-impermeable, membrane (GPM). Herein, we introduce a highly sensitive, colourimetric-based, plastic film sensor for the measurement of both gaseous and dissolved CO₂, in which a pH-sensitive dye, thymol blue (TB) is coated onto particles of hydrophilic silica to create a CO₂-sensitive, TB-based pigment, which is then extruded into low density polyethylene (LDPE) to create a GPM-free, i.e. naked, TB plastic sensor film for gaseous and dissolved CO₂ measurements. When used for making dissolved CO₂ measurements, the hydrophobic nature of the LDPE renders the film: (i) indifferent to ionic strength, (ii) highly resistant to acid attack and (iii) stable when stored under ambient (dark) conditions for > 8 months, with no loss of colour or function. Here, the performance of the TB plastic film is primarily assessed as a dissolved CO₂ sensor in highly saline (3.5 wt%) water. The TB film is blue in the absence of CO₂ and yellow in its presence, exhibiting 50% transition in its colour at ca. 0.18% CO₂. This new type of CO₂ sensor has great potential in the monitoring of CO₂ levels in the hydrosphere, as well as elsewhere, e.g. food packaging and possibly patient monitoring.

Key words: thymol blue, LDPE, extrusion, carbon dioxide, optical sensor, salt water
1. Introduction
Carbon dioxide (CO$_2$) is a key parameter in many biological and biochemical processes [1-3] and so it follows that the measurement of CO$_2$ is important in many different fields [4-7], not least of which is the monitoring of dissolved CO$_2$ in the hydrosphere, i.e. oceans, river, lakes and streams [1, 8-10].

Many different methods have been used to measure CO$_2$ in air and in water, including: gas chromatography [11], titrimetry [12], coulometry [13], amperometry [14], potentiometry (including ISEs and ISFETS) [6,15,16], UV/Vis spectrophotometry [17,18] and IR spectrometry [19]. Obviously, any methods that require reagents, regular sample taking and/or pumps are inappropriate for long-term, in-situ deployment, and under such circumstances solid state sensors, such as optodes [20] and potentiometric devices [6,15,16,21,22] appear more appropriate.

The most commonly used sensor for dissolved CO$_2$ measurements is the Severinghaus electrode [6, 15], which comprises a pH electrode in contact with a thin layer of bicarbonate buffer solution, with the whole system encapsulated by a thin, gas-permeable, but ion-impermeable membrane (referred to henceforth as a 'GPM'), such as PTFE. In a Severinghaus electrode, a change in the ambient level of dissolved CO$_2$ produces a change in the pH of the bicarbonate layer, which is detected by the encapsulated pH electrode. However, the Severinghaus electrode is usually quite bulky and susceptible to electrical interference.

There has been increasing interest over the last 24 years in solid-state, CO$_2$-sensitive optical sensors [23-25]. Such sensors, like the Severinghaus electrode, are usually based on the acidic nature of dissolved CO$_2$, and use an embedded fluorescent, or colourimetric, pH sensor to detect the CO$_2$-induced pH change in the sensor layer. The most popular of these solid-state optical sensors employs a quaternary ammonium hydroxide salt, Q+OH$^-$.xH$_2$O, (a phase transfer agent) to create a solvent-soluble version of the deprotonated form of the pH indicating dye, D$, i.e. Q$^+$.D$^-$.xH$_2$O, which can then be incorporated in a solvent-based ink, containing a lipophilic polymer, which, in turn, can be cast onto an inert substrate, such as glass or Mylar$^\text{®}$, to yield a CO$_2$-sensitive optical film.
The general mechanism of the above phase transfer optical CO$_2$ sensor [23-25], referred to henceforth as a 'PT CO$_2$ sensor', is summarised by the following reaction equation,

$$Q^+D^- \cdot xH_2O + CO_2 \rightleftharpoons Q^+HCO_3^- \cdot (x-1)H_2O + DH \quad (1)$$

in which the deprotonated pH sensitive dye, $Q^+D^- \cdot xH_2O$, is reversibly protonated, when CO$_2$ is present, to form $Q^+HCO_3^- \cdot (x-1)H_2O \cdot DH$, resulting in a colour (or fluorescence) change, from A to B, which is similar to that seen in aqueous solution when the free dye, $D^-$, is protonated by an acid to form DH. The PT CO$_2$ sensor relies on the water of hydration of the ion-pair to interact with the CO$_2$ to form reversibly the lipophilic species: $Q^+HCO_3^- \cdot (x-1)H_2O$ and, simultaneously, the differently coloured/fluorescent species, DH. The CO$_2$-sensitivity of the PT CO$_2$ sensor can be adjusted by varying the base concentration and by using pH indicating dyes with different $pK_a$'s. Not surprisingly, given reaction (1), this type of sensor responds equally well to dry and humid CO$_2$-containing gases.

The attractions of using such optical sensors for CO$_2$, rather than the Severinghaus electrode for example, include: (1) freedom from electrical interference, (2) easily miniaturised, (3) ideal for remote sensing, (4) rapid in response, (5) inexpensive and simple to make and, (6) usually disposable [25]. A major weakness of the PT CO$_2$-optical sensor is a low stability when placed in direct contact with water, since this often leads to: (i) leaching of the pH-sensor dye, particularly in high ionic strength, i.e. salty, water and (ii) proton interference, especially under acidic conditions (i.e. usually pH < 4). As a result, although there have been many reports of PT gaseous CO$_2$ sensors, there are relatively few for dissolved CO$_2$, especially in salty or acidic solution. In general, those that have been reported for such work combine a PT gaseous CO$_2$ sensor with a surface coating of a GPM, such as PTFE or silicone.

A list of some of the reported different solid-state, dissolved CO$_2$ PT optical sensors is given in table 1, along with short notes regarding their formulation, sensitivity and storage stability.
Table 1: Examples of solid-state, PT dissolved CO₂ optical sensors

<table>
<thead>
<tr>
<th>Type</th>
<th>dye</th>
<th>base</th>
<th>Encapsulation medium/ gas permeable membrane</th>
<th>%CO₂ (S=1/2)</th>
<th>storage</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour-based</td>
<td>MCP</td>
<td>TOAH</td>
<td>EC/EC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.00</td>
<td>up to 2 days</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>borate/ bicarbonate</td>
<td>HS water/silicone</td>
<td>0.01</td>
<td>&gt;4 days</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>BTB</td>
<td>TOAH</td>
<td>ionic liquids (RTILs)/none</td>
<td>60.00</td>
<td>1 month</td>
<td>28</td>
</tr>
<tr>
<td>Fluorescence-based</td>
<td>HPTS</td>
<td>TOAH</td>
<td>EC/Teflon</td>
<td>0.30</td>
<td>several days</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>HPTS</td>
<td>TOAH</td>
<td>silicone/silicone</td>
<td>10.00</td>
<td>over 5 months</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>HPTS</td>
<td>TOAH</td>
<td>EC/EC</td>
<td>0.6&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>&lt;5 days</td>
<td>31, 32</td>
</tr>
</tbody>
</table>

MCP: meta-cresol purple; TB: thymol blue; BTB: bromothymol blue; HPTS: 8-hydroxypyrene-1,3,6-trisulfonate; TOAH: tetraoctylammonium hydroxide; EC: ethyl cellulose; HS water: highly saline water; <sup>a</sup>: only stable when pH≥6 and ionic strength ≤ 0.01M; <sup>b</sup>: based on dual-lifetime referencing (DLR); <sup>c</sup>: characterised in gaseous CO₂.

From the entries in table 1 it is clear that most reported solid state PT dissolved CO₂ sensors utilise a GPM in order to prevent dye leaching and/or protonation by the solution under test. Interestingly, an exception appears to be the fluorescent-based, PT dissolved CO₂ sensor sold currently by PreSens GmbH [31,32], which appears to be sold in a naked, i.e. GPM free, form. However, and perhaps not surprisingly, the manufacturer reports that the latter displays 'cross-sensitivity to ionic strength (salinity)' and cannot be used at 'pH above 10 or below 4'. It is worth noting here too that a quite different optical sensor for CO₂ has been reported recently, which uses a highly selective carbonate ionophore, coupled to a highly basic pH sensor, encapsulated in a polymeric film [20]. The latter responds well to CO₂ in both air and dissolved in water, but suffers chloride interference when used in sea water and cannot be used much below pH 4.8 [20,22]. Consistent with most work on other CO₂ optical sensors, the authors suggest that these problems may be avoided by adding a GPM layer to the optical sensor [20].
As indicated by the data in table 1, another common drawback exhibited by many PT CO₂ sensors is an inherent short shelf-life, probably due to the presence of other acidic gases, such as SO₂ or NO₂ in the atmosphere, that irreversibly protonate the sensor film [31]. Other, more recent, work shows that ambient humidity and sensor film water content are also important factors in determining PT CO₂ sensor shelf-life, and that usually the higher the relative humidity the greater the shelf-life [30]. These shelf life issues, and the apparent need for special storage conditions, represent a barrier to the large-scale commercialisation of the PT CO₂ sensor technology.

In a recent paper, this group reported on a naked, i.e. no GPM layer, low density polyethylene (LDPE) plastic fluorescence-based PT CO₂ sensor [33], created by blending, in an extruder, the LDPE with a CO₂-sensitive pigment, comprising a coating of the fluorescent, pH-sensitive, dye (HPTS) on hydrophilic, fumed silica. The sensor film was studied mainly as a sensor for gaseous CO₂, but some additional preliminary work revealed it to be very stable and functional when used directly, i.e. in its naked form, in aqueous solution to monitor dissolved CO₂. In addition, the HPTS-LDPE film appeared very stable when stored under ambient conditions in the dark.

Here we describe the results of a more substantial study of the optical sensing of dissolved CO₂, using an extruded, naked, plastic, colour-based, solid-state PT CO₂ sensor, since, unlike fluorescence, absorbance changes can be readily detected by eye and monitored inexpensively using digital camera technology, coupled with RGB analysis [34]. The study is focussed largely on the measurement of dissolved CO₂ in highly saline water, i.e. under conditions that are usually considered operationally highly challenging, if not impossible, for all naked CO₂ optical sensors.

### 2. Experimental

#### 2.1. Materials

In this work, Thymol Blue (TB) was chosen as the colour-based CO₂ sensor dye, as it has found widespread use in this role, due to its moderate \( pK_a \) (= 8.9), striking colour change (blue in its deprotonated form, TB\(^+\), and yellow in its protonated form, HTB) and low cost.
The thymol blue sodium salt (TB) was purchased from Sigma Aldrich (95%, 861367-5G), and used as received, as was the water-soluble base, tetrabutyl ammonium hydroxide, TBAH, 40 wt% in water, i.e. Q\(^+\)OH\(^-\)\cdot xH_2O, where Q\(^+\) = tetrabutyl ammonium cation. The latter was used to create the ion-pair, Q\(^+\)D\(^-\)\cdot xH_2O, in reaction (1), where D\(^-\) is TB\(^-\), which was then coated onto particles of hydrophilic fumed silica, Aerosil 130, a gift from Evonik (BET surface area = 130 ± 25 m\(^2\) g\(^{-1}\)), so as to create the PT-based, CO\(_2\) -sensitive TB-pigment, *vide infra*.

The low-density polyethylene, LDPE, used to make the plastic films, was supplied by PW Hall UK in powder form, melt flow index, MFI, 20, for masterbatch manufacture, and the LDPE pellets (MFI = 4), for final film production, were provided by Ultrapolymers UK. All gases used were high purity and included pure CO\(_2\) and Ar. Individual mixtures of: (i) 5% CO\(_2\)/air, (ii) 1% CO\(_2\)/air mixture and (iii) 0.1% CO\(_2\)/air were purchased from BOC and used as received. Gas mixtures with other loadings of CO\(_2\) were generated using a Cole Parmer gas blender, which allowed a chosen CO\(_2\)/air mixture, i.e. (i), (ii) or (iii) described above, to be blended with Ar. For CO\(_2\) work in which the gas had a relative humidity (RH) of 100%, the CO\(_2\)-containing gas under test was sparged through two Drechsel bottles, both half-full with water, connected in series, before exposure to the CO\(_2\) sensor. In this work, highly saline water is used, and referred to throughout as 'HS\(^1\)' water, and contained 3.5 wt% NaCl (i.e. 0.60 M), which is that usually found in seawater.

2.2. TB pigment preparation

0.2 g of TB were fully dissolved in the mixture of 3 ml of a 40% TBAH aqueous solution and 100 ml of ethanol in a 250 ml round-bottomed flask. 2 g of hydrophilic silica were then added, and the mixture stirred for 2.5 h, after which the solvent was removed under reduced pressure using a rotary evaporator. The final, dry blue TB pigment powder in the round-bottomed flask was then ground into a fine powder using a mortar and pestle. The above process produces hydrophilic silica particles coated with the blue Q\(^+\)D\(^-\)\cdot xH_2O, salt, where Q\(^+\) = tetrabutyl ammonium cation and D\(^-\) is the deprotonated form of the thymol blue, TB\(^-\), referred to throughout as the TB pigment. The indicator film coating on the silica particles is due to physical adsorption only. The TB-pigment appears blue in the absence of 100% CO\(_2\), and yellow in its presence, as illustrated by the photographs of the two different forms of the TB pigment powder in Fig. 1.
2.3. TB plastic sensor film fabrication

The CO$_2$-sensitive TB plastic film was fabricated via the extrusion of a mixture of the TB-pigment with low-density polyethylene (LDPE), thereby producing a final pigment loading of 5 wt%, using a Rondol Microlab 10 mm twin screw extruder (barrel L/D 25/1). Thus, 2 g TB-pigment and 18 g LDPE powder (melt flow index, MFI, 20) were mixed to produce 10 wt% pigmented powder, which was then extruded as a 2 mm diameter 'string' of a 10 wt% of TB pigmented LDPE master-batch, which was fed into an on-line pelletiser to create 3 mm long pellets. The above production method used a processing temperature that increased gradually from 90°C at the feed zone, to 140°C at the die, and a pigment/LDPE mixture feed hopper rate of 41 rpm. The extruder screw speed was 80 rpm and the pelletizer speed was 0.5 m min$^{-1}$.

The 3 mm long masterbatch pellets were then ‘diluted’ by 50% w/w using the LDPE pellets (MFI 4), to produce the final 5 wt% TB pigment in LDPE loading required for the final extruded TB–LDPE film. The thermal processing conditions for producing the TB pigmented LDPE extruded film, i.e. the ‘TB– film’, were: 90°C (at the feed zone), increasing to 110–125–135°C (across the barrel) and finally 140°C (at the die zone). The feed hopper rate was 20 rpm, the extruder screw speed was 80 rpm, and the extruded film take-off speed was 1.7 m min$^{-1}$. The final plastic film product, a 5 wt% pigmented TB plastic film (central thickness 47.5 ± 2.5 μm), was blue/green-coloured in the absence of CO$_2$, indicating the dye was in its deprotonated, TB$^-$, form, but rapidly turned yellow upon exposure to a stream of CO$_2$, due to the formation of HTB. Photographs of the film in these two different states are illustrated in Fig. 2.
Fig. 2. Extruded TB plastic film (from left to right) in the absence (in Ar) and presence of CO₂.

The batch to batch reproducibility of the film manufacture was > 95%, as was the reproducibility within a batch, and in both cases this appears to be due mainly to small variations in film thickness; thus, if produced on a commercial scale these small variances would be reduced much further.

2.4. Measurements

All UV/Vis absorbance measurements were made using an Agilent Technologies CARY 60 UV-vis spectrophotometer and all diffuse reflectance spectra were recorded using a KONICA MINOLTA Spectrophotometer (CM-2500d). Unless stated otherwise, all experiments were conducted at 21°C and, before any absorbance measurements were made, the spectrophotometric cell, containing the TB film, was flushed with the CO₂-containing gas under test for at least 15 min.

When used as a dissolved CO₂ sensor, the TB plastic film was always pre-soaked in the HS water for at least 24 h before use, since, during this time the background absorbance of the film increased a little (Δabsorbance, at λ = 513 nm = 0.09) due to a slight haziness, due to the uptake of water by the film. No further changes were observed in the film after this 24 h period, even when stored in HS water for weeks. When used as a dissolved CO₂ sensor, the soaked TB plastic film was placed in a spectrophotometer cell containing the HS water and the CO₂-containing gas, of known composition, was then bubbled gently (flow rate = ca. 0.2 ml s⁻¹) through the cuvette via a syringe needle for at least 45 min, to ensure full equilibration, before any absorbance measurements were made. In the study of the effect of temperature on the sensitivity of the TB sensor towards dissolved CO₂, temperature control was achieved using a thermostatted cuvette holder.
3. Results and discussion

3.1. Theory

The TB plastic film CO\textsubscript{2} indicator comprises a classic PT colourimetric CO\textsubscript{2}-sensitive ink coating on hydrophilic silica particles that are embedded in a film of LDPE. A schematic of the key features of the TB plastic film is given in Fig. 3, including the identification of the main reaction species involved in the colour-changing process, as summarised by reaction (1). As noted earlier, in all the work described here, the TB plastic film used had NO additional GPM, i.e. they were always used in its, as produced, i.e. naked, form. From Fig. 3 it is clear that by embedding the indicator in the highly hydrophobic LDPE, the latter acts not only as the encapsulation material but as an intrinsic GPM, rendering redundant the need for an external GPM coating, as favoured by most optical sensors for dissolved CO\textsubscript{2}, and so simplifying the fabrication of a PT colorimetric CO\textsubscript{2}-sensitive sensor for such work.

![Fig. 3. Schematic of the key features and reactions of a naked, i.e. no additional GPM, extruded TB plastic film, comprising an LDPE film pigmented with hydrophilic silica particles coated with Q\textsuperscript{+}TB\textsuperscript{-}.xH\textsubscript{2}O salt, where Q\textsuperscript{+} = tetrabutyl ammonium cation.](image)

Given the TB-based CO\textsubscript{2} sensor pigment particles, embedded in the LDPE, are a classic example of a PT CO\textsubscript{2} indicator, with a response based on reaction (1), it is worthwhile identifying the usual terms and equations used to describe the response of such a sensor. For example, the general parameter, \(R\), is the ratio of the concentrations of the protonated to deprotonated forms of the dye, and is calculated using the experimentally measured absorbance, for a colour-based CO\textsubscript{2} sensor at a known %CO\textsubscript{2}, made at the wavelength of maximum absorbance for \(D^-\) alone, i.e. absorbance \((A)\) at \(\lambda_{\text{max}}(D^-)\). Thus,
\[ R = \frac{(A_0 - A)}{(A - A_\infty)} = \frac{[HD]}{[D^-]} \]  

(2)

where \([HD]\) and \([D^-]\) are the concentrations of the protonated and deprotonated forms of the dye, respectively. \(A_0\) is the value of absorbance due to the dye at \(\lambda_{\text{max}}(D^-)\) when \(\%\text{CO}_2 = 0\) (i.e. when all the dye is in its deprotonated form) and \(A_\infty\) is the absorbance of the film when all the dye is in its protonated form, HD, i.e. when \(\%\text{CO}_2 = \infty\). In this work, a value for the latter was obtained by exposing the indicator to 100% CO\(_2\). Combining equation (2) with an expression for the equilibrium constant for reaction (1), it follows that:

\[ R = \frac{[HD]}{[D^-]} = \alpha \times \%\text{CO}_2 \]  

(3)

where \(\alpha\) is a proportionality constant (units: \(\%^{-1}\)) which is directly related to the equilibrium constant for reaction (1) and provides a measure of the sensitivity of the CO\(_2\) optical sensor under test [35]. Other work shows that the value of \(\alpha\) is inversely dependent upon the background base concentration, \([Q^+\text{OH}^- \cdot x\text{H}_2\text{O}]\) [25,26], as well as dye \(pK_a\) and temperature [24,36,37].

A more accessible, direct measure of the sensitivity of a CO\(_2\) optical sensor is provided by the value of the \(\%\text{CO}_2\) at which the normalised optical signal, \(S\), is equal to \(\frac{1}{2}\) and \(R = 1\), henceforth referred to as \(\%\text{CO}_2(S=1/2)\). At the \(\%\text{CO}_2(S=1/2)\) for an indicator film, the concentrations of the protonated and deprotonated forms of the dye are the same, \(R = 1\) and so, from eqn (3), \(\%\text{CO}_2(S=1/2) = 1/\alpha\). It is more convenient to use \(\%\text{CO}_2(S=1/2)\) values to compare the sensitivities of different CO\(_2\) sensors, than refer to their calculated values of \(\alpha\), and, clearly, the lower the value of \(\%\text{CO}_2(S=1/2)\) for CO\(_2\) sensor based on reaction (1), the greater its sensitivity.

3.2. The TB-pigment

The diffuse reflectance spectra of a sample of the TB-pigment powder under an argon (i.e. 0% CO\(_2\)) and 100% CO\(_2\) were measured using a Minolta diffuse reflectance spectrometer. In making these measurements, 4 g of the TB-pigment were placed in a 14 ml glass vial with a plastic cap, and the gases under test, i.e. either pure Ar or CO\(_2\), were then purged through the vial for 2 min before recording the diffuse reflectance spectra of the pigment. The results of this work are illustrated in Fig. 4 and reveal that the TB-pigment has UV/Vis
absorption peaks at 620 nm in the absence of CO₂ (due to its deprotonated, TB⁻, blue/green form) and at 440 nm in the presence of CO₂ (due to its protonated HTB yellow form). The CO₂-induced colour changes were very fast (< 1 s) and reversible.

Fig. 4. Kubelka Munk diffuse reflectance spectra of the TB pigment powder (as illustrated in Fig. 2) under 0 (blue line) and 100% of CO₂.

3.3. The TB plastic film: gaseous CO₂

The absorbance spectrum of the TB plastic film was studied as a function of the ambient level of gaseous CO₂ (0% to 100%) and the results are illustrated in Fig. 5.
Fig. 5. UV-vis absorbance spectra of thymol blue plastic film recorded when exposed to different %CO₂/Ar gas phase compositions. The %CO₂ levels used were (from top to bottom): 0, 0.1, 0.3, 0.4, 1 and 100%.

From the data in Fig. 5 it is clear the absorbance exhibited by the deprotonated form of the TB plastic film, D⁻, (λ_max = 621 nm) decreases with increasing %CO₂ in the ambient gas stream, as TB⁻ is converted to HTB, via reaction (1). A plot of the absorbance at λ_max = 621 nm, as a function of %CO₂, gleaned from the spectra illustrated in Fig. 5, is illustrated in Fig. 6, along with a plot of R vs %CO₂ as the insert diagram, where R was calculated using eqn(2) and the absorbance data in the main diagram. The latter plot reveals a value for %CO₂(S=1/2) = 0.063%, which suggests that the TB plastic film is extremely sensitive to the ambient level of gaseous CO₂ and more sensitive than many other reported similar PT-based CO₂ sensors (see table 1). The limit of detection, LOD, was calculated as 0.006% CO₂.

When the CO₂-containing purge gases used above were saturated with water vapour, i.e. 100% RH, and passed over a TB plastic film, the λ_max for the TB⁻, in the TB plastic film, underwent a hypsochromatic shift from 621 nm to 613 nm, and the film appeared ca. 3x’s less sensitive towards CO₂, i.e. %CO₂(S=1/2) = of 0.20%, with an LOD of 0.01%.
Fig. 6. Plot of absorbance of a TB film at 621 nm versus %CO$_2$ in the dry gas stream. The insert plot of the data in the main diagram, in the form of $R$, see eqn (2), vs %CO$_2$ reveals a good straight line with a gradient (= $\alpha$) = 15.9%$^{-1}$ and thus a %CO$_2$(S=1/2) value of 0.063%.

Although the exact cause for the marked decrease in the CO$_2$ sensitivity of the TB plastic film in humid air (and – it turns out – in HS water too, *vide infra*) is not clear, it is likely to be associated with a change in the microenvironment surrounding the LDPE encapsulated TB-ink coated silica pigment particles due, in turn, to an increased water content of the film. Evidence for this is provided by: (i) the observation of a slightly increased haziness in the film ($\Delta$absorbance ($\lambda = 513$ nm) = 0.09) and (ii) the shift in the absorbance $\lambda_{max}$ for the TB film from its usual value of 621 nm for a dry film, to 613 nm in humid air (and 603 nm in HS water). The latter is particularly interesting as the absorbance $\lambda_{max}$ for TB$^{-}$ dissolved in water is ca. 596 nm. This finding suggests that, notwithstanding the presence of the highly hydrophobic LDPE, the TB pigment particles take up sufficient water vapour from the ambient humid gas phase to render their microenvironment almost water like. The effects produced by an increase in polarity of the microenvironment, signified by the negative shift in the value for $\lambda_{max}$ for a dry TB plastic film, brought about by the presence of a high (100%) RH or immersion of the TB film into HS water, are likely to include: (i) a decrease in the $pK_a$ of TB and (ii) a decrease in the solubility of CO$_2$ (for example the solubility of CO$_2$ is 17 times
higher in trichloromethane than it is in water) [38]. Both of these effects are likely to produce a measurable decrease in the CO₂ sensitivity exhibited by the TB film when highly hydrated, as opposed to dry. It is also worth noting that this overall loss of sensitivity, brought about by a high ambient RH or immersion of the film in HS water, is readily reversed by returning the TB plastic film to a dry atmosphere.

The ability of the TB plastic film to respond to a sudden and striking change in %CO₂ was investigated using an alternating stream of 0% (i.e. Ar) and 1% CO₂. The results of this work revealed that, in the gas phase, the sensor exhibits a 90% response time (t₅₀↓) of ca. 3 min, and a 50% recovery time (t₅₀↑) of ca. 32 min. Thus, compared to the TB pigment, and most conventional, ink-based, CO₂ optical sensors (typical t₅₀↓ & t₅₀↑ times of: 4 and 7 s ) [33], the TB plastic film has relatively long response and recovery times in making gas phase CO₂ measurements. However, this is not too surprising given that the TB plastic film is much thicker, i.e. ca. 47.5 ± 2.5 µm, than that of most ink-based CO₂ sensors (1-8 microns). The response and recovery times of most CO₂ optical sensors depend directly upon the rate of diffusion of the CO₂ into and out of the sensor film, with a proportionality constant that is inversely proportional to the square of the film thickness [39]. Thus, by using a narrower film die to extrude the film it should be possible to create sufficiently thin TB plastic film (say 15 µm) to compete with the low t₅₀↓ & t₅₀↑ times exhibited by most CO₂ sensor ink films [33].

For comparison purposes, a classic solvent-based, naked PT TB ink film sensor for CO₂ was made according to a previously-reported recipe [26] and its sensitivity towards CO₂ was then assessed as described above for the TB plastic film. The TB ink film (comprising TB in ethyl cellulose, with TBAH as the base and tributylphosphate as the plasticiser) exhibited a similar sensitivity and LOD towards gaseous CO₂, i.e. %CO₂(S=1/2) = 0.08% and 0.001%, respectively, as that of the TB plastic film, i.e. %CO₂(S=1/2) = 0.06% and 0.01%. Note that here, and elsewhere [26], work shows that the TB ink film has a very limited stability when used to detect dissolved CO₂ and fails within minutes, when placed in aqueous solution with a pH < 6 or an ionic strength > 0.01 M. As a result it is entirely inappropriate for making any dissolved CO₂ measurements and, its response is consistent with the fact that many of the
CO$_2$ sensor ink films listed in table 1 require an additional GPM layer in order to allow them to monitor dissolved CO$_2$.

3.4. The TB plastic film: dissolved CO$_2$ sensor

In this work a pre-soaked TB plastic film was placed in a cuvette containing HS water. Different, known levels of CO$_2$, spanning the range 0-100% CO$_2$, were then bubbled through the HS water for at least 45 min to ensure complete saturation, after which, in each case, the UV/Vis absorption spectrum of the film was recorded.

![UV-vis absorbance spectra of a typical TB film in HS water saturated with the following different percentages of CO$_2$ (from top to bottom): 0, 0.1, 0.3, 0.4, 0.6, 1 and 100%.](image)

The results of this work are illustrated in Fig. 7 and reveal that, as expected, the absorbance of the TB film due to TB$^-$, with a $\lambda_{max}$ value = 603 nm, decreases with increasing %CO$_2$. A plot of the absorbance at 603 nm vs %CO$_2$ data, along with an the insert plot of $R$ vs %CO$_2$, are illustrated in Fig. 8 and the latter reveals a good straight line, in accordance with eqn (2), with a gradient ($\alpha$) = 5.6 %$^{-1}$, i.e. a %CO$_2$(S=1/2) value of 0.18%, which is very similar to that exhibited by the TB plastic film when in a humid (100% RH) gas phase. The LOD for CO$_2$ for
the TB film in HS water was the same as that in humid gas, i.e. 0.01%, showing that the TB film is as sensitive towards CO₂ in HS water as it is in humid gas.

Fig. 8. Plots of absorbance of TB plastic film in HS water at 603 nm versus %CO₂. Insert plot of $R$, derived from the absorbance date in the main plot and eqn (2), vs % CO₂ yields a line of best fit with a gradient $= \alpha = 5.6 \%^{-1}$.

The following sections describe the results of further probing of the characteristics of the TB plastic film in monitoring dissolved CO₂ levels in HS water.

3.5. Effect of temperature

Reaction (1), the underlying process behind all PT-based CO₂ optical sensors, including the TB plastic film reported here, is spontaneous and involves a decrease in system entropy, as the gaseous CO₂ reacts with the $Q^+D^-xH_2O$ ion-pair, to form a bicarbonate salt. From basic thermodynamics, it follows that the equilibrium constant for reaction (1), a measure of which is the value of $\alpha$, will decrease with increasing temperature, as predicted by the van’t Hoff reaction isochore. Thus, all PT-based CO₂ optical sensors are temperature sensitive, and decrease in CO₂ sensitivity with increasing temperature [24,25]. The TB plastic film
reported here is no exception, as revealed by the results of a series of calibration curves (i.e. absorbance vs %CO$_2$ curves) recorded at different temperatures, spanning the range 0-31°C in HS water. The latter data were used to generate the appropriate $R$ vs %CO$_2$ plots for the different temperatures studied, illustrated in Fig. 9, from which values of the gradient for the different temperatures, i.e. $\alpha(T)$, were determined. An Arrhenius plot of this data, i.e. $\ln(\alpha(T))$ vs $1/T$, revealed an activation energy for reaction (1) for the TB plastic film CO$_2$ sensor of 21.1 ± 4.2 kJ mol$^{-1}$ which is similar to that of 26.8 ± 1.0 kJ mol$^{-1}$ reported [40] by others for a TB-Ru(bpy)$_3^{2+}$ based FRET CO$_2$ sensor (polymer: ethyl cellulose; phase-transfer agent: TOAH).

![Graph showing R vs %CO$_2$ plots for different temperatures.](image)

**Fig. 9.** $R$ vs %CO$_2$ plots of thymol blue plastic film in HS water under different temperature, from top to bottom: 0.6, 11.3, 21.8, 30.7°C.

### 3.6. Storage in air

One of the most striking features of the TB plastic film is its stability in air. For example, when stored under ambient atmospheric conditions, in the dark, the film is stable for > 8 months, showing no loss in sensitivity. In contrast, and as illustrated by the photographs in the supplementary information, Fig. S1, a typical TB solvent-based CO$_2$ sensitive ink film lasts only ca. 4-5 days under the same conditions, before losing its blue/green colour and changing to its yellow protonated form. As noted earlier, the lack of stability exhibited by many PT-based CO$_2$ ink film sensors is usually attributed to a loss of water (if kept in a dry}
atmosphere) and possible permanent reaction with common, albeit low level, acidic pollutants, such as SO\textsubscript{2} and NO\textsubscript{2} [31]. Others have noted that the stability of the latter films can be improved markedly by storing them either in water [30], in a very humid (usually RH \text\geq ca. 80\%) atmosphere [41], or with sodium carbonate (as a sink for volatile acidic volatiles) in the dark [40]. Obviously, the need for such storage conditions then places a constraint on the commercial potential of such CO\textsubscript{2} ink film sensors, whereas, in contrast, the TB plastic film sensor reported here appears very stable when stored under ambient, dark conditions. However, these films, as with most dye-containing sensor films, will photobleach with time if left exposed to sunlight for long periods of time, thus the need for dark storage conditions.

3.7. Drift in HS water

In order to probe the stability, and functionality, of the TB film in HS water further, a typical TB film was placed in a 1 cm cuvette filled with HS water and stored in 0.1% saturated CO\textsubscript{2} water for over 7 days. The HS water was flushed once every day with 1% CO\textsubscript{2}, before being returned to a background 0.1% CO\textsubscript{2} saturation level and the absorbance of the TB plastic film, at 600 nm, monitored throughout. The results of this work are illustrated in Fig. 10 and show that in HS water the film’s sensitivity (towards CO\textsubscript{2}) remains high and shows little evidence of dye leaching over a 7 day period, with a drift in initial absorbance of \textless 0.3\% per day.
Fig. 10. Plots of absorbance of thymol blue plastic film in HS water alternatively purged through 0.1% CO₂ and 1% CO₂, and repeated for 7 days.

From this work the calculated 50% response $t_{50\downarrow}$ (0.1% to 1% CO₂) and 50% recovery (1% to 0.1% CO₂) $t_{50\uparrow}$ times for the TB plastic film, when used for dissolved CO₂ measurements, were 5 min and 15 min, respectively. These response and recovery times are obviously completely inadequate for the monitoring of rapid changes in dissolved CO₂, as required for blood gas monitoring for example, where the %CO₂ is typically 5%. A Severinghaus electrode for example is often able to respond in a minute, although this can be considerably longer if it possesses a large volume internal bulk electrolyte, or if the concentrations of CO₂ are low [22,42,43]. For example, Xi and Bakker [22] report that, for a shift in CO₂ saturation from 0.04% to 0.66%, the Severinghaus probe takes at least 5 min to stabilise to its new potential. Interestingly, this is the probe's 'response time', as the concentration of CO₂ has been increased, and it follows, from the work of others [42,43], that the associated recovery time for the probe will be longer, possibly by a factor of 4, which implies a recovery time of ca. 20 min. Note that the CO₂ saturation values used by Xi and Bakker [22] (0.04% to 0.66%) in their work on a Severinghaus electrode are not too dissimilar to those used here for the
TB film (0.1% to 1%) in Fig. 11, which suggests that the 47.5 μm, TB plastic film has a similar response time, and probable recovery time, very similar to that of the Severinghaus electrode used by Xi and Bakker [22], when responding to these very low levels of CO₂. However, in order to demonstrate that the TB plastic film can be made to respond much faster simply by making it thinner, a 15 μm, as opposed to the usual 47.5 μm, TB plastic film was prepared and subjected to the same alternative purging in HS water as described in Fig. 10. This short study showed that the thin film exhibits the same sensitivity, i.e. same value for α, but much shorter with t_{50\downarrow} (0.1% to 1% CO₂) and t_{50\uparrow} (1% to 0.1% CO₂) times of 2 min and 6 min, than the thick film sensor. The latter response and recovery times appear reasonable, if only for use in long-term monitoring of CO₂ levels in aquatic systems, but open for further improvement.

3.8. Stability in acidic solution

Another striking advantage of the TB plastic film CO₂ sensor over most other naked optical CO₂ sensors, is its marked high-stability when used in very acidic (pH ≤ 2) solution. As noted earlier, most 'naked' optical CO₂ sensors, including the commercial PreSens GmbH, fluorescent-based, dissolved CO₂ sensor, cannot be used for any significant period of time at pH's < 4 [32]. In contrast, the TB plastic film sensor reported here shows no loss of function, or dye, when stored in 0.01 M HCl aqueous solution for at least for 3 hours. Evidence of the ability of the TB plastic film to function as a CO₂ sensor in aqueous solution, regardless of pH, is provided by the series of photographic images illustrated in the supplementary information, Figs. S2 and S3. From this work, it is clear that upon dipping the TB film into sparkling, i.e. carbonated, water, the TB⁻, in the TB plastic film is readily protonated (green/blue to yellow), within 1 min, and its original colour is restored upon its removal from the sparkling water. As illustrated by the pictures in Fig. S3 show that when the same TB plastic film is placed in a 0.01 M HCl aqueous solution the film's green colour remains unaltered, but changes to yellow, via reaction (1), upon bubbling CO₂ through the solution. When the yellow TB film is withdrawn from the aqueous acidic solution, it regains its original green colour within minutes.
Other work showed that the TB plastic film was unresponsive to pH when placed, for at least 1 h, in HS water with its pH adjusted to either: 8.4, 6.4, 4.3 or 2.3, thereby providing additional evidence that the TB plastic film responds to dissolved CO₂ and not pH.

From the results of this work, it appears that the LDPE acts both as a sensor pigment encapsulation medium and an intrinsic GPM, protecting the sensor TB pigment particles from dye leaching and acid attack. As a consequence, the TB plastic film sensor is easier and less expensive to construct than most reported optical sensors for dissolved CO₂ detection.

4. Conclusions

Table 2 below provides a summary of the main results reported here for all the CO₂ sensors/environments tested, i.e. (a) the TB plastic film in: (i) a dry and wet (RH = 100%) gas phase and (ii) HS water and (b) a TB ink film in a dry gas phase, reported above. These results include: the measured absorbance $\lambda_{max}$ values (due to TB$^+$), CO₂ sensitivity values (i.e. $\alpha$ and %CO₂(S=1/2) values), and associated limits of detection (LOD) values for all the CO₂ sensors/environments. An inspection of these results shows that the TB plastic film is ca. 3x's more sensitive when used to detect the 100% dry gaseous CO₂ than dissolved or humid CO₂. In addition, it can be seen that the TB plastic film is similar in sensitivity to that of a conventional TB ink film, when used to detect gaseous CO₂. The results in HS water are particularly remarkable given that the TB plastic film has no additional GPM, and yet is an effective, stable and highly sensitive sensor for CO₂ in this highly saline medium. In addition, it appears able to tolerate high levels of acidity and has a long storage lifetime when kept in the dark, but otherwise ambient conditions, in contrast with most other PT-based optical sensors for CO₂ (see table 1). Like many CO₂ optical sensors, the TB plastic film’s CO₂ sensitivity decreases with increasing temperature ($\Delta H = 21.1 \pm 4.2$ kJ mol$^{-1}$).
Table 2: Absorbance and response characteristics of the TB based CO₂ sensors reported in this work

<table>
<thead>
<tr>
<th>TB Sensor</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>R</th>
<th>α (%)&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>%CO₂ (S=1/2)</th>
<th>LOD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB plastic film in dry gas</td>
<td>621</td>
<td>79.8</td>
<td>15 ± 2</td>
<td>0.06</td>
<td>0.006</td>
</tr>
<tr>
<td>TB plastic film in 100% humid gas</td>
<td>613</td>
<td>22.0</td>
<td>4.4 ± 0.1</td>
<td>0.20</td>
<td>0.01</td>
</tr>
<tr>
<td>TB plastic film in HS water</td>
<td>603</td>
<td>23.0</td>
<td>5.6 ± 0.1</td>
<td>0.18</td>
<td>0.01</td>
</tr>
<tr>
<td>TB solvent-based ink film in dry gas</td>
<td>626</td>
<td>62.8</td>
<td>12.5 ± 0.3</td>
<td>0.08</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The CO₂ sensitivity of the current TB film (%CO₂(S=1/2) = 0.18% = 1800 µatm) is a little too high for monitoring the usual level of dissolved CO₂ found in sea water (ca. 0.035%). However, there are many instances in the hydrosphere where relevant higher levels are found including: eutrophic lakes (87% of Florida lakes have supersaturated levels of CO₂) [44,45], ocean depths (at which significant CO₂ sequestration occurs) [46] and fish farms [47,48]. By choosing a different pH-sensor dye with a higher pKₐ, a more sensitive CO₂ sensor could be constructed and vice versa [37]. And, by making the film much thinner, the indicator may find application in areas where the rapid monitoring of CO₂ is required, such as in the rapid analysis of clinical blood samples or the rapid depth profiling of aquatic systems.

Acknowledgements

We thank the DAFM for funding this work (FIRM project ref: 11/F/015)
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