

Development of novel thermochromic plastic films for optical temperature sensing

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The preparation of plastic film optical 'CO₂-based' temperature-sensing films that utilise the temperature-dependent acid–base equilibria of indicator dyes is described. In film formulations a suitable dye, such as phenolphthalein, in a hydrophobic base, tetraoctylammonium hydroxide, solubilised within a plasticised, hydrophobic polymer matrix, creates a system which is sensitive to ambient CO₂ levels. The resultant solution, when cast on to glass supports, yields 'CO₂-based' temperature-sensitive films which change colour in response to a highly temperature-dependent reaction between the deprotonated form of the dye and CO₂ dissolved in the film. The absorbance characteristics of these films display a fully reversible response to temperature over a temperature range which is largely determined by the pK_a of the dye and the ambient CO₂ concentration. The magnitude of the response is dependent on the dye concentration. The response time towards changes in temperature is typically ≤2.2 min and the films show good stability under operational conditions. A simple mechanism of the reaction is suggested and an associated working equation has been derived and fitted to data obtained for a typical sensor functioning over the range 278–333 K. A 'CO₂-based' temperature-sensing film is used successfully alongside a standard CO₂ sensing film. This combination not only provides temperature information but also ensures that the response of the CO₂ sensor is corrected for any changes in temperature. In addition, both sensors use the same interrogating light and light intensity monitoring system because they contain the same phenolphthalein dye. The latter two features represent an improvement on the existing optical systems used to measure CO₂ and temperature.

1. Introduction

Considerable work has focused on the development of optical sensors for the quantitative detection of a wide range of analytes, including gases, ionic species and biomolecules.^{1,2} Another parameter which is of considerable biological and commercial importance and which often needs to be measured concurrently with the above species is temperature, and this also lends itself to measurement using optical sensors. Where temperature is to be measured at the same time as another analyte, it is advantageous to use the same method of detection for both as this reduces the complexity of the instrumentation required.³ A range of optical sensors^{4–6} recently developed for analyte detection in areas such as blood gas analysis, bioreactor monitoring and modified atmosphere packaging utilise a pH-sensitive absorbance- or fluorescence-based indicator which detects the analyte by interacting with acidic or basic species in the sample. The use of the same measurement technique (*i.e.*, absorbance or fluorescence) and, if possible, the same sensor unit for temperature measurements would therefore be useful, especially where temperature is known to affect the sensor's response to the other analyte of interest and so needs to be continuously monitored.

Several groups^{7–9} have utilised the temperature sensitivity of pH indicator–buffer systems to develop optical thermometers. Most of these rely on the temperature sensitivity of the pK_a of the buffer component, usually tris(hydroxymethyl)aminomethane (TRIS), which has a particularly high ΔpH/ΔT coefficient (−0.015 °C^{−1}).⁸ This is coupled to the pH sensitivity of a dye to produce a measurable optical response. An early example is the work by Bowie *et al.*,⁸ who used TRIS and the pH indicator cresol red to prepare an aqueous temperature-indicating solution for monitoring intra-cuvette temperatures in clinical analysers.

Straub and Seitz³ developed this idea further in their design of a fibre optic-based temperature sensor which also utilised the temperature sensitivity of the pK_a of TRIS. In this sensor, the acid–base indicator dye phenol red was immobilised in a cross-linked polyacrylamide matrix which was soaked in an aqueous solution of TRIS buffer. This was used as the basis of a semi-solid state sensor which was capable of making remote temperature measurements.

Both of these approaches exploited the temperature sensitivity of TRIS buffer coupled with a pH-sensitive indicator dye to produce an optical response. However, many dyes themselves display marked temperature sensitivity and the thermochromism of pH-sensitive indicators has been well documented.^{10,11} This thermochromic behaviour results from the temperature dependence of the acid–base equilibrium



where DH and D[−] are the protonated and deprotonated forms of the dye, respectively, and K_{a,T} is the acid dissociation constant for the dye at temperature T.

We have found that dyes of this type, when ion-paired to a suitable phase transfer agent, may be readily incorporated into hydrophobic polymers to yield thin, effectively solid state films.^{4,5} Such films have been successfully used, in their pH-sensing capacity, to produce optical sensors for the detection of acid gases such as carbon dioxide, which is the principle acid gas found in air and an important analyte in medical monitoring. These pH indicator-based, optical CO₂ sensors change colour in response to a reversible change in the local pH induced by CO₂ as it interacts with the film. As in solution, the pH equilibria set up in these polymer films, and hence their response to CO₂, are highly temperature dependent. In general, an increase in temperature decreases the sensitivity of such sensors toward

CO₂. In their role as CO₂ sensors this cross-sensitivity is a problem and such film sensors are generally thermostated at a constant temperature to overcome it. It may be envisaged, however, that if, instead of keeping the temperature constant, the level of CO₂ in the environment surrounding the sensor is kept constant, the sensor can be transformed into a novel temperature sensor or optical thermometer.

In this paper, the development and characterisation of solid state thin film optical thermometers based on the temperature sensitivity of the reaction of pH indicator dyes with ambient CO₂ is described. A model is presented which allows the behaviour of such sensors to be predicted quantitatively and the possibility of the simultaneous measurement of both an analyte gas (in this case CO₂) and temperature using essentially the same sensing unit is investigated.

2. Experimental

2.1 Materials

Ethylcellulose (ethoxyl content 46%), tributyl phosphate, tetraoctylammonium bromide and the dyes phenolphthalein, thymol blue and *m*-cresol purple were obtained from Aldrich Chemicals (Gillingham, Dorset, UK). A 0.5 mol dm⁻³ tetraoctylammonium hydroxide solution in methanol was prepared from the corresponding bromide solution using wet silver oxide to effect the ion exchange.¹² The gases used, N₂ and a 5% CO₂-N₂ blend, were of high purity (>99%) and were purchased from BOC, Guildford, Surrey, UK. The solvents used to make up the various solutions were of high purity and were purchased from Aldrich Chemicals.

2.2 Preparation of sensing films

The temperature-sensing polymer film sensors had the general composition: indicator dye-phase transfer agent-polymer-plasticiser-glass support. The phase transfer agent, tetraoctylammonium hydroxide (TOAOH), serves both to solvate the hydrophilic indicator dye anion in the hydrophobic polymer matrix and to provide the trace water required to allow dissolution of CO₂ in the film. The plasticiser, tributyl phosphate, is present to improve the gas permeability of the film. The standard temperature-sensitive plastic film sensor used in this work contained phenolphthalein as the dye. Film solutions were prepared by adding 5 mg of phenolphthalein to 1.25 cm³ of methanolic TOAOH (0.5 mol dm⁻³) and then adding a further 0.5 cm³ of methanol. This was then added to 5 cm³ of a 10% (m/v) solution of ethylcellulose in toluene-ethanol (80 + 20). Finally, 0.5 cm³ of the plasticiser, tributyl phosphate, was added and the film solution was stirred thoroughly. This gave a final dye concentration in the film solution of 2.2 × 10⁻³ mol dm⁻³. Where other dyes were used, the quantity added was adjusted to give the same molarity. The final solvent-free films were prepared by casting the film solutions on to glass microscope cover-slips through a 100 μm thick brass template with a rectangular hole (0.8 × 1.5 cm). Films were left to dry overnight at ambient temperature and were subsequently stored in a desiccator. Calculations based on the known area and mass of the films gave film thickness estimates of 15–20 μm.

2.3 Instrumentation

UV/VIS absorption spectra and single wavelength absorption measurements were recorded using a Lambda 3 double beam scanning spectrometer (Perkin-Elmer, Norwalk, CT, USA) and a Model 8625 single beam spectrometer (Unicam, Cambridge,

UK). The glass cover-slips on to which the films had been cast were taped on to a 1 cm thick cylindrical glass vessel equipped with water inlet and outlet tubes. Temperature control was achieved by pumping water from a thermostated water-bath through this vessel using a Grant SU6 thermostat unit (Grant Instruments, Cambridge, UK). A Grant Type CC25 cooling unit was used where temperatures below room temperature were required. Where concentrations of CO₂ other than atmospheric were required, the appropriate blend was generated using a gas blender (Model 852VI-B, Signal Instruments, Camberley, Surrey, UK). Computer modelling was performed using a Jandel Scientific (San Rafael, CA, USA) curve fitting program.

3. Theory

It is useful first to consider the simple case of a pH-sensitive dye dissolved in water and buffered at a fixed proton concentration, [H⁺]_{fixd}. In aqueous solution the dye can exist in both a protonated and a deprotonated form (DH and D⁻) and the relationship between the relative concentrations of these two species is determined by the equilibrium reaction (1). *K*_{a,T}, the acid dissociation constant for the dye at the temperature of the experiment, is then defined as follows:

$$K_{a,T} = \frac{[D^-][H^+]_{\text{fixd}}}{[DH]} \quad (2)$$

The value of *K*_{a,T} will vary with temperature

$$K_{a,T} = K_{a,T=\infty} \cdot \exp(-\Delta H^\circ/RT) \quad (3)$$

where Δ*H*[°] is the change in standard enthalpy for equilibrium reaction (1) and is invariably > 0 and *K*_{a,T=∞} is the value of *K*_{a,T} at infinite temperature [*K*_{a,T=∞} = exp(Δ*S*[°]/*R*)].

Often the UV/VIS absorption spectra of DH and D⁻ are completely different; typically the wavelength of maximum absorption of DH is much less than that of D⁻, *i.e.*, λ_{max}(DH) < λ_{max}(D⁻). In many cases this difference in UV/VIS absorption spectra is such that the molar absorptivity of DH at λ_{max}(D⁻) is approximately zero and, under these conditions, any absorbance measurements made at λ_{max}(D⁻), *i.e.*, *Abs*(D⁻)_T, reflect solely the concentration of D⁻ in the aqueous solution at temperature *T* and [H⁺]_{fixd}. If we assume that such a situation holds for the dye in reaction (1), it follows from eqns. (2) and (3) and Beer's law that

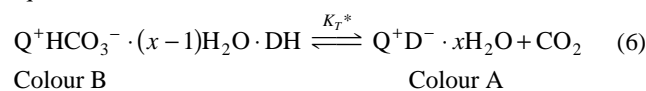
$$K_{a,T}/[H^+]_{\text{fixd}} = \frac{(K_{a,T=\infty}/[H^+]_{\text{fixd}})\exp(-\Delta H^\circ/RT)}{Abs(D^-)_T/[Abs(D^-)_{T=\infty} - Abs(D^-)_T]} \quad (4)$$

where *Abs*(D⁻)_{T=∞} is the absorbance of the aqueous solution at infinite temperature, at which imaginary point all the dye will be fully deprotonated, *i.e.*, *Abs*(D⁻)_{T=∞} is a direct measure of the total dye concentration, where [dye]_{total} = [D⁻] + [DH], assuming the UV/VIS absorption spectrum of D⁻ does not change with temperature. A value of *Abs*(D⁻)_{T=∞} can be gleaned through a knowledge of the original total dye concentration, [dye]_{total}, and the molar absorptivity of D⁻ at λ_{max}(D⁻), ε(D⁻), since *Abs*(D⁻)_{T=∞} = [dye]_{total}·ε(D⁻) × pathlength. It follows from eqn. (4) that the experimentally measurable parameter *Abs*(D⁻)_T is related to the temperature of the aqueous solution as follows

$$[Abs(D^-)_T]^{-1} = \frac{\exp(\Delta H^\circ/RT)[H^+]_{\text{fixd}}/[K_{a,T=\infty}]}{Abs(D^-)_{T=\infty} + [Abs(D^-)_{T=\infty}]^{-1}} \quad (5)$$

In earlier work,^{10,11} a pH buffer was used to achieve a 'fixed' pH. However, not surprisingly, the pH of the buffer is also temperature dependent, [*i.e.*, [H⁺]_{fixd,T} = [H⁺]_{fixd,T=∞} exp(-Δ*H*[°]_{buff}/*RT*), where Δ*H*[°]_{buff} is usually > 0], and as a result, the observed value for Δ*H*, Δ*H*_{obs}, as determined using a suitably modified version of eqn. (5), will be the difference in Δ*H*, for the indicator and the buffer, *i.e.*, Δ*H*[°]_{obs} = Δ*H*[°] - Δ*H*[°]_{buff}.

In our work using thin plastic films for sensing carbon dioxide, the pH-sensitive dye is solubilised using a phase transfer agent, Q^+OH^- , into the hydrophobic medium of the encapsulating plastic medium. However, the pH-sensitive dye is still able to reflect a change in the pH of the surrounding medium and change colour when exposed to CO_2 . The key equilibrium reaction is as follows



where $Q^+HCO_3^- \cdot (x-1)H_2O \cdot DH$ and $Q^+D^- \cdot xH_2O$ are the lipophilic forms of the protonated and deprotonated forms of the dye, with very similar UV/VIS absorption spectral characteristics to DH and D^- , respectively. K_T^* is the equilibrium constant for the overall process at temperature T and is directly related to the acid dissociation constant for the dye, *i.e.*, $K_{a,T}$. The overall process, reaction (6), is in fact a combination of the equilibrium reaction involving dissolved CO_2 and the deprotonated dye and the equilibrium reaction between dissolved CO_2 and the CO_2 in the gas phase.

In the past, when using plastic films as optical sensors for CO_2 at a fixed temperature, T , any variation in the ambient partial pressure of CO_2 , P_{CO_2} , can be detected by monitoring $Abs(D^-)_{T, \text{film}}$, the absorbance at $\lambda_{\text{max}}(D^-)$ of the film at ambient temperature. In the present work, where these films are used as temperature sensors, it is the partial pressure of ambient CO_2 which is fixed. Under these conditions, when the ambient temperature is varied, the films should behave in a manner similar to that for a pH-sensitive dye in aqueous solution, in which the $[H^+]$ is fixed, and the key equation relating the observed absorbance due to D^- encapsulated in the film, $Abs(D^-)_{T, \text{film}}$, and temperature will be similar to that of eqn. (5), *i.e.*,

$$[Abs(D^-)_{T, \text{film}}]^{-1} = \frac{\exp(\Delta H^\circ_{\text{obs}}/RT)P_{CO_2, \text{fxd}}/[K^*_{T=\infty}]}{Abs(D^-)_{T, \text{film}^*} + [Abs(D^-)_{T, \text{film}^*}]^{-1}} \quad (7)$$

where $K^*_{T=\infty}$ is the value of K^*_T at infinite temperature, $\Delta H^\circ_{\text{obs}}$ is the enthalpy change for the overall process and $Abs(D^-)_{T, \text{film}^*}$ is the absorbance of the film when all of the dye is in the form of D^- . From eqn. (7), it follows that the sensitivity of the film at any temperature, *i.e.*, $dAbs(D^-)_{T, \text{film}}/dT$, is given by the expression

$$\frac{dAbs(D^-)_{T, \text{film}}}{dT} = \frac{(\Delta H^\circ_{\text{obs}}/RT^2)\beta \cdot \exp(\Delta H^\circ_{\text{obs}}/RT)}{\{\beta \cdot \exp(\Delta H^\circ_{\text{obs}}/RT) + [Abs(D^-)_{T, \text{film}}]^{-1}\}^2} \quad (8)$$

where

$$\beta = P_{CO_2, \text{fxd}}/K^*_{T=\infty} \cdot Abs(D^-)_{T, \text{film}^*} \quad (9)$$

A useful rough guide to a temperature around which the particular thermochromic sensor, based on the above CO_2 -sensitive plastic films, will operate is $T(S = \frac{1}{2})$, the temperature at which $Abs(D^-)_{T, \text{film}}$ is 50% of its maximum value, *i.e.*, when $Abs(D^-)_{T, \text{film}} = Abs(D^-)_{T=\infty, \text{film}}/2 = Abs(D^-)_{T, \text{film}^*}/2$. Under these conditions, it can be shown from eqn. (7) that $T(S = \frac{1}{2})$ is related to the experimental parameters $P_{CO_2, \text{fxd}}$, $K^*_{T=\infty}$ and ΔH° as follows:

$$T(S = \frac{1}{2}) = \frac{\Delta H^\circ_{\text{obs}}}{R \ln(K^*_{T=\infty}/P_{CO_2, \text{fxd}})} \quad (10)$$

From eqn. (10), it follows that this type of thermochromic sensor will operate at lower $T(S = \frac{1}{2})$ values if (a) the dye is changed to one with a lower pK_a (since K^*_T is related directly to the acid dissociation constant for the dye) or (b) if the initial, fixed partial pressure of carbon dioxide, $P_{CO_2, \text{fxd}}$, is decreased. From a combination of eqns. (8) and (10), the following expression for the film sensitivity, at $T(S = \frac{1}{2})$, can be derived:

$$[dAbs(D^-)_{T, \text{film}}/dT]_{T(S = \frac{1}{2})} = R \cdot Abs(D^-)_{T, \text{film}^*} [\ln(K^*_{T=\infty}/P_{CO_2, \text{fxd}})]^2 / 4 \Delta H^\circ_{\text{obs}} \quad (11)$$

If this model applies to our system, various predictions can be made based on these equations. From eqn. (11), it follows that the sensitivity of a film at $T(S = \frac{1}{2})$ can be increased by (i) changing to a dye with a larger $K_{a, T=\infty}$, *i.e.*, one with a lower pK_a , (ii) decreasing the initial, fixed partial pressure of carbon dioxide, $P_{CO_2, \text{fxd}}$, or (iii) increasing the initial dye concentration [which will increase $Abs(D^-)_{T, \text{film}^*}$]. In addition, eqn. (7) can be rearranged to the following form:

$$Abs(D^-)_{T, \text{film}} = 1/[\beta \exp(\alpha/T) + \gamma] \quad (12)$$

where $\alpha = \Delta H^\circ_{\text{obs}}/R$, $\beta = P_{CO_2, \text{fxd}}/K^*_{T=\infty} Abs(D^-)_{T, \text{film}^*}$ and $\gamma = [Abs(D^-)_{T=\infty, \text{film}^*}]^{-1}$; α is in units of K^{-1} and β and γ are both unitless. It follows from eqn. (12) that from experimental data of the form $Abs(D^-)_{T, \text{film}}$ vs. temperature, values for α , β and γ , which are characteristic of the film, can be extracted. In the following section the model and its associated equations are tested using experimental data for a series of different film temperature sensors.

4. Results and discussion

4.1 Temperature response of a phenolphthalein film in atmospheric $[CO_2]$

A thin plasticized ethylcellulose film containing the indicator dye phenolphthalein was prepared and its temperature sensitivity was investigated. This dye has a high pK_a (9.6)¹³ and at room temperature and atmospheric CO_2 levels (3×10^{-4} atm) it is almost exclusively in its protonated, colourless form. As the temperature of the film was raised an absorption peak gradually developed at 573 nm. Increasing the temperature drives the equilibrium reaction (6) more to the right, thereby increasing the concentration of the deprotonated form of the dye, which is deep pink. These spectral changes are illustrated in Fig. 1. Further work showed that the response of the film was fully reversible over many cycles between 305 and 345 K (32–70 °C). Above a temperature of 343 K for a prolonged period (> 30 min), the film became permanently coloured, probably owing to thermal destruction of the base, tetraoctylammonium hydroxide. Cycling the temperature between the physiologically important range 295 and 318 K (which experimentally is achieved in 15 s) gave a 90% response and recovery time of 2.2 and 1.0 min, respectively.

In order to extract values for α , β and γ a set of absorbance values obtained at 573 nm for the film over the range 305–345 K were fitted to eqn. (12). Fig. 2 shows the experimentally determined data points and the line passing through them represents the least-squares line of best fit of the data to eqn.

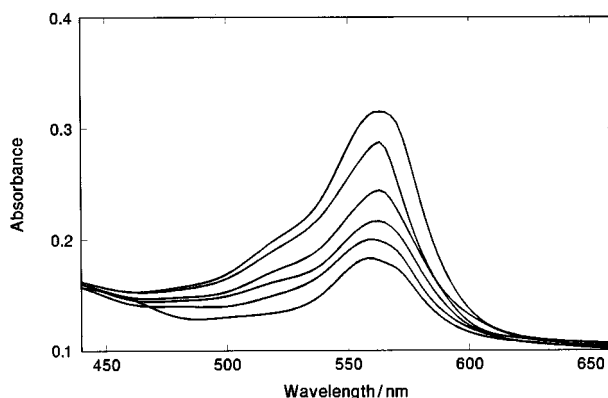


Fig. 1 Effect of temperature on the absorption spectrum of a phenolphthalein-ethyl cellulose film. Temperature (from top to bottom): 308, 311, 314, 317, 321 and 324 K.

(12). This line of best fit yielded values for α , β and γ of 6.65×10^3 K, 5.62×10^{-9} and 1.93, respectively.

From the optimised value for α obtained from this work, a ΔH° value of 55.3 kJ mol^{-1} was calculated for this reaction, which falls into the ΔH° range $31\text{--}71 \text{ kJ mol}^{-1}$ and which has been reported previously for dye protonation reactions.^{4,14} In all subsequent work, pH-sensitive dyes of a similar nature were used and the key reaction (6) was the same. As a result, the value of ΔH obtained from the value of α , *i.e.*, 55.3 kJ mol^{-1} , was used in all of the model calculations and optimisations as it is likely to be the same for all of the systems studied. To check that this assumption was reasonable, some optimisations were also re-run without inputting this value as a constant, thereby allowing the optimisation program to generate its own value for α . When this was done, the value for ΔH obtained was always very close to 55.3 kJ mol^{-1} .

The value of γ yields a value of $Abs(D^-)_{T, \text{film}^*}$ of 0.52, which agrees reasonably well with the value of 0.58 calculated from a knowledge of initial dye concentration, the film thickness and the molar absorptivity of D^- at its λ_{max} . The slight discrepancy between $Abs(D^-)_{T, \text{film}^*}$ and the calculated film absorbance may arise because the molar absorptivity used in the latter was for the D^- in aqueous solution not the encapsulating medium. The latter probably differs slightly from that associated with the anionic form of the dye, now in the form of an ion pair, $Q^+D^- \cdot xH_2O$, in a plastic film environment.

The optimised values of α , β and γ in eqn. (12) allows a complete $Abs(D^-)_{T, \text{film}}$ versus temperature plot over an extended temperature range to be constructed for the phenolphthalein-ethylcellulose film. The inset in Fig. 2 shows this calculated profile together with the data points from which it was derived. It should be stressed that this full curve is not intended to represent the operational capabilities of the sensing film, which is restricted to the relatively narrow range 305–345 K, but rather illustrates the overall shape predicted by the mathematical function in eqn. (12).

4.2 Effect of local P_{CO_2} , pK_a of the dye and initial dye concentration

In a series of additional experiments, the effects of changes in local P_{CO_2} , pK_a of the dye and initial dye concentration on the absorbance versus temperature profiles of the temperature film sensors were investigated. Eqn. (12) predicts that altering the former two parameters will affect the value of the variable β , while altering the latter will affect the value of γ .

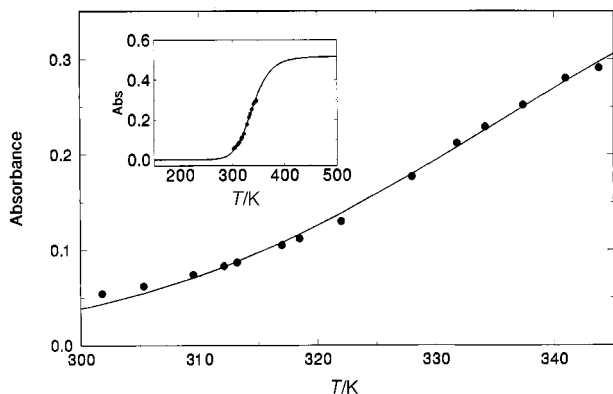


Fig. 2 Absorbance versus temperature plot of a phenolphthalein-ethylcellulose film. The line through the experimentally determined data points represents the least-squares line of best fit calculated using eqn. (13). Optimised values of α , β and γ were $\alpha = 6.65 \times 10^3$, $\beta = 5.62 \times 10^{-9}$ and $\gamma = 1.94$. The inset represents the theoretical curve over an extended temperature range calculated using eqn. (13) and values of α , β and γ obtained from the main diagram.

Fig. 3 shows the effect of four different P_{CO_2} levels on the temperature sensitivity of a standard phenolphthalein film. The data points were experimentally determined and the lines through them represent the lines of best fit to these data points determined using eqn. (12), $\alpha = 6.65 \times 10^3$ K and optimised values of γ and β . As expected from eqn. (12), an increase in P_{CO_2} resulted in an increase in the value of β , and the $Abs(D^-)_{T, \text{film}}$ versus temperature profiles were shifted to higher temperatures, *i.e.*, $T(S = 1/2)$ increased. As predicted by eqn. (9) of the model, a plot of the optimised values of β versus P_{CO_2} (shown in the inset to Fig. 3) is a good straight line.

The pK_a of the indicator dye used was also varied and the results of this work are illustrated in Fig. 4. The choice of dye was limited to those with a suitable pK_a for making measurements at atmospheric levels of CO_2 . Hence the two phthalein dyes phenolphthalein ($pK_a = 9.6$)¹³ and *o*-cresolphthalein ($pK_a = 9.4$)¹⁵ and the sulphonphthalein dye thymol blue ($pK_a = 9.0$)¹⁶ were used. From the results in Fig. 4 it can be seen that as the pK_a of the indicator was decreased the value of β decreased and, as a consequence, $T(S = 1/2)$ decreased. Eqn. (12) predicts a linear inverse relationship between the K_a of the dye and β and

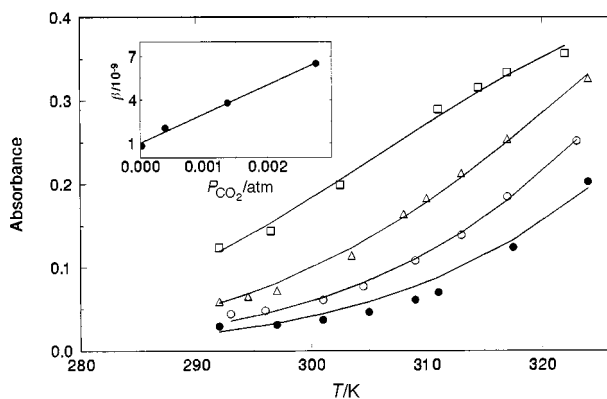


Fig. 3 Effect of P_{CO_2} on experimentally determined absorbance versus temperature plots. P_{CO_2} values were 2.00×10^{-5} (●), 3.90×10^{-4} (○), 1.37×10^{-3} (△) and 2.76×10^{-3} (□) atm. The lines through the experimentally determined data points represent the least-squares line of best fit calculated using eqn. (13) and taking $\alpha = 6.65 \times 10^3$. The optimised β and γ values obtained were 8.17×10^{-10} , 1.96 (●), 2.05×10^{-9} , 1.32 (○), 3.78×10^{-9} , 1.00 (△) and 7.47×10^{-9} , 1.26 (□). The inset shows a plot of β versus P_{CO_2} using optimised β values obtained from plots in the main diagram.

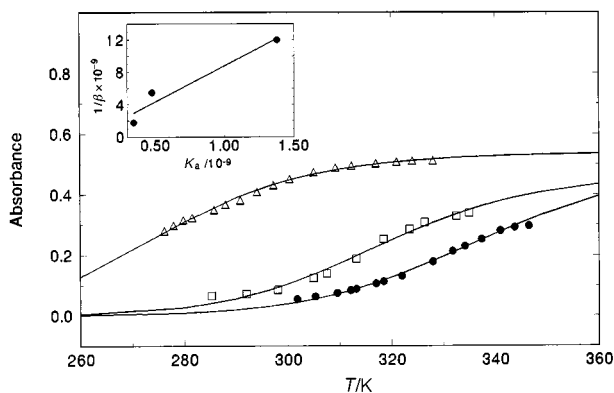


Fig. 4 Effect of dye pK_a on experimentally determined absorbance versus temperature plots. The dyes used were phenolphthalein (●), *o*-cresolphthalein (□) and thymol blue (△). The lines through the experimentally determined data points represent the least-squares line of best fit calculated using eqn. (13) and taking $\alpha = 6.65 \times 10^3$. The optimised β and γ values obtained were 5.62×10^{-9} , 1.94 (●), 1.84×10^{-9} , 2.08 (□), 6.45×10^{-11} , 1.93 (△). The inset shows a plot of $1/\beta$ versus dye K_a values using optimised β values obtained from plots in the main diagram.

this appears to be confirmed by the data plot of $1/\beta$ versus dye K_a (inset in Fig. 4).

Fig. 5 illustrates the results of a study of the effect of the initial dye concentration on the absorbance versus temperature profiles of a series of films which used the same dye, phenolphthalein. From these data it can be seen that raising the initial dye concentration did not affect the position of the profile, *i.e.*, $T(S = 1/2)$ remained unchanged, but did increase the total absorbance change observed. As a result, the temperature sensitivity of such sensors, $dAbs(D^-)_{T, \text{film}}/dT$, increased with increasing amount of dye [*i.e.*, increasing $Abs(D^-)_{T, \text{film}}$]. From eqn. (12) of the model, a linear relationship between $1/\gamma$ and $Abs(D^-)_{T, \text{film}}$ was expected and found, as illustrated by the plot of the data in the inset Fig. 5.

From these results, it appears that the model applies well to this system and that it may be used to make both qualitative and quantitative predictions about the response characteristics of this type of temperature-sensing film.

4.3 Simultaneous measurement of temperature and CO₂

As already stated, pH-sensitive films which have been designed for monitoring analytes such as CO₂ are frequently thermostated to avoid interference from temperature sensitivity. This may not always be desirable, however, owing to factors such as cost, accessibility and ease of miniaturisation. As it is easy to correct the response of such sensors for temperature effects, thermostating might be avoided if a reliable temperature-sensing element could be incorporated into the unit.

Experiments showed that the temperature-sensing film (in which a fixed level of CO₂ was encapsulated by a gas-impermeable membrane) could be readily used next to a CO₂-sensing film which utilised the same dye, *i.e.*, *m*-cresol purple. Both films could be interrogated using the same optics. The temperature-sensing film provided the necessary information to correct any change in response in the CO₂ sensing film due to a change in ambient temperature over the range tested, *i.e.*, 298–318 K. The attractive feature of this system is the use of the same optical system to provide both temperature and P_{CO_2} data using two simple, similar optical sensors.

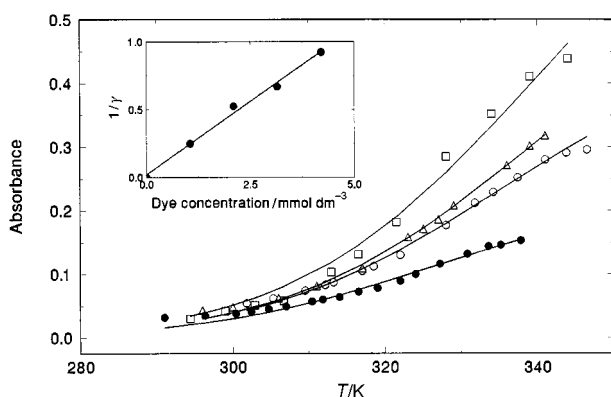


Fig. 5 Effect of dye concentration on experimentally determined absorbance versus temperature plots. Dye concentrations: 1.05 (●), 2.10 (○), 3.15 (△) and 4.20 (□) mmol dm⁻³. The lines through the experimentally determined data points represent the least-squares line of best fit calculated using eqn. (13) and taking $\alpha = 6.65 \times 10^3$. The optimised β and γ values obtained were 6.86×10^{-9} , 4.02 (●), 5.62×10^{-9} , 1.94 (○), 5.54×10^{-9} , 1.48 (△) and 4.29×10^{-9} , 1.08 (□). The inset shows a plot of $1/\gamma$ versus dye concentration using optimised γ values obtained from plots in the main diagram.

5. Conclusions

A 'CO₂-based' temperature-sensing film has been developed and the parameters affecting its response characteristics have been quantified. It has been used successfully alongside a standard CO₂-sensing film to monitor both temperature and P_{CO_2} simultaneously using the same interrogating and monitoring system. The reliability of the sensor for CO₂ detection has been demonstrated many times in previous papers.^{4,17} Most commonly, IR spectroscopy is used to confirm the reliability of the CO₂ sensor. In the work described in this paper, mercury thermometers were used to record independently temperature and the typical absorbance versus temperature profiles illustrated were recorded several times in order to confirm their reliability and reproducibility. As noted earlier, although the films functioned well between 305 and 345 K, at temperatures above 345 K prolonged exposure caused some degree of hysteresis in the absorbance versus temperature profiles of the sensor.

In the present study, experiments were performed using variable P_{CO_2} levels provided by a gas blender and variable temperature achieved by thermostating the gas and the cell block containing the sensor elements inside the spectrometer cell compartment. However, in practice, for real environment measurements of P_{CO_2} and temperature, it is envisaged that both optical sensors (*i.e.*, the CO₂ and the 'CO₂-based' temperature sensors) would be used in combination with fibre optics as is common practice with other multi-analyte sensors.¹⁸

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7. References

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