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Optical sensor for carbon dioxide gas determination, characterization and improvements

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ABSTRACT

A study of different alternatives to improve the stability and lifetime of sensors for the determination of gaseous CO_2 has been performed. It includes the characterization of different sensing membranes, a discussion of the results obtained and possibilities for the future. The solid sensor membrane for gaseous CO_2 based on changes in the luminiscence of a luminophore immobilized on O_2-insensitive film, concurrent with the displacement of a pH indicator, has some drawbacks, such as the loss of efficiency over time and the need to maintain the sensor in special atmospheric conditions. As a solution to these drawbacks, two alternatives were tested, the first alternative was replacing the newly proposed tetraoctyl ammonium hydroxide (TOAOH) phase transfer agent with other basic agents that did not undergo a Hoffman degradation reaction, and the second alternative was the use of hydrophilic polymers that could retain water needed for CO_2 sensing more efficiently. The different membranes tested indicated that the use of tetramethyl ammonium (TMAOH) instead of TOAOH as the phase transfer agent produced better results regarding stability and sensitivity. In addition, replacing the membrane polymer with hydrophilic polymers improved the sensing characteristics in terms of response time and stability over hydrophobic polymers. With a detection limit of 0.006%, the response time is 19 s and the recovery time is 100 s. The lifetime of the sensing membranes, which do not need to be held in any special atmosphere other than darkness, is longer than at least 300 days for membranes with TMAOH in hydrophilic polymer and 515 days for membranes with TMAOH in ethyl cellulose.

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1. Introduction

The determination of CO_2 gas is of considerable interest in different areas including clinical [1,2], environmental [3], biological [4], biochemical and industrial fields [5], such as wastewater treatment, biotechnological process control and modified atmosphere packaging [6]. Conventional optical sensors for CO_2 gas are based on the measurement of IR absorption extending from 4200 to 4400 nm, but they are bulky and expensive, and the interference from CO is serious, because CO has very similar absorption behaviours to CO_2 in the IR spectral region. Further, optical monitoring of CO_2 concentration based on its acidic nature, using the colorimetric or luminescence changes in acid–base indicators located in a membrane in an aqueous hydrogen carbonate buffer, has been studied [7,8]. The limitations of this design due to the need to maintain the moisture level in the membrane enable the production of solid sensor membranes [7] that can replace the aqueous buffer system with a quaternary ammonium hydroxide, typically TOAOH. This base performs various functions: 1) ion pairing of the basic form of the pH indicator, depending on the charged groups of the indicator; and 2) providing needed water from the hydrated ionic pair for the uptake of CO_2 from the atmosphere by forming a lipophilic hydrogencarbonate buffer [9].

The main problems with this type of sensor are the limited number of fluorescent indicators that allow for such measures [10]. In order to eliminate this problem, different strategies have been devised such as fluorescence resonance energy transfer [11] and inner filters like photoinduced electronic transfers [12] and protonic transfers [13–15].

Other problems related to the poor photostability of the indicators, variability of the excitation source and the leaching of reagents have been addressed through lifetime measurement [16] instead of the intensity measurement, by methods of ratios of signals or ratiometric using, for example, two excitation wavelengths of luminophore [4,17], and a dual luminophore referencing technique (DLR) [18].

The membrane polymer used plays an important role in the sensitivity and stability of gas sensors, with ethyl cellulose [19], sol–gels [11], silicones [4] and composite materials [20] being common. The sensing material can also be placed on a rigid and optically transparent support [18] or directly attached to the tip, at the end or in the core of an optical fibre [1]. The problems of

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stability with membranes, especially with regard to dehydration, have been addressed through the replacement of a quaternary ammonium cation with room-temperature ionic liquids [21,22]. The use of ionic liquids in gas sensor carbon dioxide helps to retain water [23]. The most recent modification with this type of sensor is the use of upconverting nanoparticles (UCNOs) [24] that exhibit high penetration depth with the excitation power, with the advantage of avoiding any autofluorescence from biomolecules because of the excitation by infrared radiation.

In this paper, we report on some strategies to reduce the inconvenience of solid phase sensors, exemplified by a phosphorescent inner filter-based sensor for CO_2 [25]. The sensor works by quenching a luminescent dye using one of the chemical forms of a non-fluorescent pH indicator, α-naphtholphthalein [26] containing the ammonium quaternary hydroxide TOAOH as an internal buffering system. The change in the position of the acid–base equilibrium by CO_2 in the membrane and the consequent change in colour is transduced in luminescence change due to the overlapping of the absorbance spectrum of the pH indicator and the emission of the long-lifetime luminophore platinum octaethylporphyrin (PtOEP). The first alternative tested was replacing the widely-used TOAOH by other basic agents, since these did not undergo Hoffman degradation, and the second alternative was the use of hydrophilic polymers [27] that could retain water molecules needed for CO_2 sensing more efficiently.

2. Experimental section

2.1. Materials

The polymers used for the membrane preparation were: poly (vinylidene chloride-co-vinyl chloride) (PVCD, particle size 240–320 μm), ethyl cellulose (EC, ethoxyl content 49%) from Sigma-Aldrich Química S.A. (Madrid, Spain), and hydroxypropyl methylcellulose polymers (Methocel E-5, LV USP/EP premium grade) from Dow Chemical Iberia S.L. (Tarragona, Spain).

The other reagents used were platinum octaethylporphyrin complex (PtOEP) obtained from Porphyrin Products Inc. (Logan, UT, USA), α-naphtholphthalein, tetraoctyl ammonium hydroxide (TOAOH) (0.335 M in methanol), tetramethylammonium hydroxide pentahydrate (TMAOH), 1,8-diazabicyclo[5.4.0] undec-7-ene, n-butilamine, ethanolamine, pyridine, cetyltrimethylammonium bromide (CTAB), polyoxyethylene lauryl ether (Brig 35), dioxane, tetrahydrofuran (THF), tributyl phosphate (TBP) and Tween 20, all from Sigma-Aldrich Química S.A; Mighty PSP from Kao Chemical GmbH (Emmerich am Rhein, Germany) and Melflux 2651 from Basf Chemical Company (Tarragona, Spain). Sheets of Mylar-type polyester from Goodfellow (Cambridge, UK) were used as a support for membranes. CO_2, O_2 and N_2 gases used were of high purity ($>$ 99%) and were supplied in gas cylinders by Air Liquid S.A. (Madrid, Spain). The water used was reverse-osmosis type quality from Milli-RO 12 plus a Milli-Q purification system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

A Cary Eclipse fluorescence spectrometer (Varian Australia Pty Ltd.) was used for steady-state luminescence measurements of the sensing films with a homemade cell holder [28], measuring the membrane at 45° angle in the cell to minimize light scattering with 2.5/5.0 nm excitation and emission slits. Double membranes on the same or opposite sides of the plastic support were irradiated with excitation light from the luminophore side and the luminescence was collected from the indicator side.

Standard mixtures of CO_2 (up to 100%) in N_2 were prepared by controlling the flow rates of gases, which entered a mixing chamber using a computer-controlled mass flow controller (Air Liquid España S.A., Madrid, Spain) operating at a total pressure of 760 Torr and a flow rate between 100 and 500 $cm^3\ min^{-1}$. For the preparation of gas mixtures with a CO_2 concentration lower than 0.40%, a standard of 5% CO_2 in nitrogen was used, with the lowest CO_2 concentration tested being 0.02%. All the emission intensity measurements were carried out at room temperature. All measurements were made in triplicate, except when stated otherwise, to check for experimental errors.

2.3. Procedures

2.3.1. Sensing membrane preparation

The membranes were produced on the non-luminescent Mylar polyester substrate using a spin-coating technique. All cocktails were prepared weighing the chemicals in a 4 mL flask with a DV215CD balance (Ohaus Co., Pine Brook, NJ, USA) with a precision of ± 0.01 mg. Cocktail 1 was prepared by adding 0.5 mg PtOEP into a solution of 100 mg PVCD in 1 mL of freshly distilled THF. Cocktail 2 in all cases contained the indicator α-naphtolphthalein along with different polymers and phase transfer agents (Table 1). Different sensing films were prepared from cocktails 1 and 2 in two different configurations on the Mylar support (12 mm × 35 mm × 0.5 mm thick): a) double-membrane configuration, one over another prepared with 15 μL of cocktail 1 and, after drying in saturated THF atmosphere for 1 h, depositing 25 μL of cocktail 2 on top of the membrane and drying under vacuum for 12 h. This configuration was used in membrane B4; b) double membrane on opposite side support configuration, prepared with 20 μL of cocktail 1 and 25 μL of cocktail 2 but each one on opposites sides of the Mylar support. This was used for membranes B1 to B3. As usual, the membranes containing PtOEP in PVCD were stored in darkness for 9 days to cure them before their use [25]. The thickness of the dried membranes was calculated to be 0.8 μm for the membrane formed using cocktail 1 and 2 μm for the membrane formed using cocktail 2.

The measurement of sensing membranes phosphorescence was performed with a gate time t_g of 10 ms and a delay time t_d of 0.15 ms, with excitation and emission slit widths of 2.5 and 5 nm at $\lambda_{em} = 537$ under a stream of a mixture of dry gas.

Table 1
Composition of the different sensor membranes tested.

Membrane	TBP (%)	α-naphtolphthalein solution[a] (%)	Ethyl cellulose solution[b] (%)	TMAOH (%)	DBU solution[c] (%)	HPMC (%)	Tween 20 (%)
Membrane B1	4.9	0.56	4.8	0.97	–	–	–
Membrane B2	4.9	0.56	4.8	–	5.48×10^{-3}	–	–
Membrane B3	4.9	0.56	–	0.97	–	60	–
Membrane B4	–	0.56	–	0.97	–	2	0.31

[a] 2 mL toluene and ethanol in ratio 80:20 v/v.
[b] In 1 mL toluene.
[c] In 200 μL methanol.

2.3.2. Operational lifetime

The prepared membranes displayed mechanical stability and good adhesion to the support. The long-term stability of both the indicator and luminophore membranes was studied separately by storing the membranes in darkness without any special atmospheric conditions. We tried storing the films in wet atmospheres, but the membranes quickly lost their properties due to the hydrophilic polymers used. The stability was checked by periodically performing a short calibration for CO_2 using 5 different gas standards covering the whole range.

2.3.3. Analytical parameters

The equation used to linearize the relationship between the phosphorescence intensity and CO_2 percentage was the inverse of relative phosphorescence intensity, where I_0 and I_{100} were the intensities at 0% and 100% gaseous CO_2, versus the inverse of the CO_2 concentration (Eq. 1) as suggested by Nakamura and Amao [19], with A and B being the two proportionality constants.

$$\frac{I_{100}-I_0}{I-I_0}=A\frac{1}{[CO_2]}+B \qquad (1)$$

This equation was selected instead of others proposed [29] because of the good fit obtained.

In addition, to compare the results obtained with the different membranes, we use the $I_{100}-I_0$ parameter as a more suitable indication of the width of the measured range of the membrane, as in previous studies [2], where I_0 and I_{100} represent the measured phosphorescence intensities of the sensing film exposed to 100% nitrogen and 100% CO_2, respectively.

3. Results and discussion

The sensing chemistry for CO_2 used in this study is based on plastic solid state membranes containing a pH indicator in a basic form along with a lipophilic organic base, usually called a phase transfer agent in a hydrophobic polymer [26,30,31]. The lipophilic base – typically a quaternary ammonium hydroxide, with TOAOH being the most common [32,33] – acts as an internal buffer to both turn the pH indicator and stabilize its basic form as a hydrated ionic pair, enabling the uptake of CO_2 from the atmosphere by forming a lipophilic hydrogencarbonate buffer. The change in the acid–base equilibrium because of CO_2 in the membrane and the consequent change in α-naphtholphthalein indicator colour are transduced here into a change in the luminescence of the platinum octaethylporphyrin complex luminophore included in the membrane [25,34]. This sensor has the problems typical of dry sensors such as needing a humid atmosphere and darkness because of dye bleaching, the presence of acidic or oxidant gases in the atmosphere, and the degradation of quaternary ammonium hydroxide via the Hofmann elimination reaction [32].

Different strategies have been devised to overcome the addressed problems as outlined in Section 1. In this study we tested two ways to increase the lifetime of sensor membranes for CO_2: 1) replacing the usual phase transfer agent (TOAOH) to one that does not undergo Hofmann degradation; and 2) replacing the hydrophobic polymer (ethyl cellulose) with a more hydrophilic polymer to reduce the water loss.

The bibliography contains a proposal to replace the usual TOAOH with neutral bases containing tertiary nitrogen at the basic position, namely phosphazene bases as well as tertiary amines such as trioctylamines, tributylamine, triethylamine and triethanolamine [35]. Phosphazene-type bases show lower sensitivity than TOAOH and the basicity of ternary amines is less than that of the phosphazene base. Trioctylamine and tributylamine were not able to deprotonate the pH indicator initially. In addition, triethylamine has a high vapour pressure, which causes the evaporation of the base from the sensor layer, whereas triethanolamine also presents a lower sensitivity towards CO_2. Another alternative proposed was to replace the usual solvent-based CO_2 indicator with a water-based CO_2 indicator that is less sensitive towards CO_2, but much more stable in terms of shelf life [36].

In this work, we study two types of lipophilic bases: quaternary ammonium hydroxides and amines, namely: TMAOH and the aliphatic amines (ethanolamine and n-butilamine) and the heterocyclic amines (pyridine and 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU)). For this study different sensor membranes are prepared whose compositions are presented in Table 1.

The decomposition of tetraalkylammonium hydroxide to form an olefin and the tertiary amine is known as the Hofmann elimination. Of the different tetraalkylammonium hydroxides, the tetramethylammonium does not contain H atom in β position, which can be captured by OH-groups to form a water molecule (Fig. 1A) unlike the usual bases used in these CO_2 sensors. For that reason, it was chosen.

In order to check the possibility of using TMAOH instead of the common TOAOH, different membranes were prepared from cocktails in ethyl cellulose containing TMAOH in concentrations ranging between 6.4×10^{-5} and 7.7×10^{-5} m (7.6% and 9.2% w/w) and the behaviour against CO_2 was measured. The optimum amount of TMAOH is 6.7×10^{-5} m (8.0% w/w) (Fig. 2) with a maximum value of $I_{100}-I_0$ of 212.3, a value of the same order of magnitude as the CO_2 sensor that we proposed previously based on the same chemistry (268.7), although in the prior case special storage conditions were required [25].

We also studied the another possibility: replacing the quaternary ammonium hydroxide, TOAOH, with basic amines acting as the transfer agent phase. This option has been tested in the bibliography but not in the usual acid base indicator-based scheme for CO_2 sensing but using a solvatochromic probe in the matrix of ethyl cellulose, in which the polarity of its microenvironment is modulated by the hydrophobic amine N,N,N′-tributylpentanamidine capable of reversibly binding to CO_2 [37].

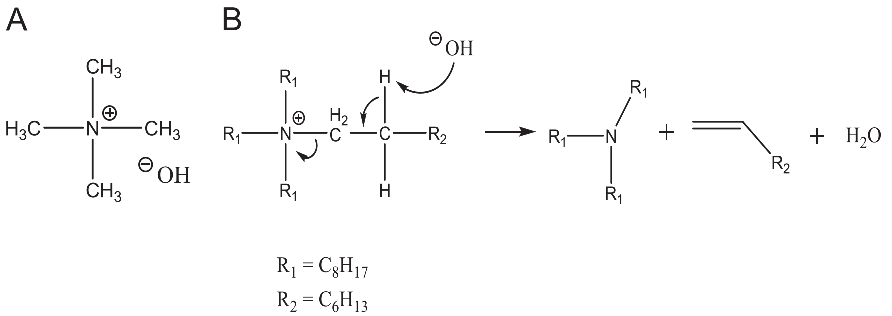

Fig. 1. (A) Chemical structure of TMAOH. (B) Reaction scheme of TOAOH.

This study selected several primary, secondary and tertiary amines with the indication of their basicity as pK_a in brackets, namely: 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (pK_a ~ 12); n-butilamine (pK_a ~ 10.59); ethanolamine (pK_a ~ 9.50) [38] and pyridine (pK_a ~ 5.25) [39]. Different cocktails were prepared with these amines but only the DBU amine was suitable to prepare membranes with good mechanical properties that were homogenous, transparent, and had a good response to CO_2. In order to study the influence of DBU on membrane properties and the response to CO_2, membranes containing different amounts of DBU, from 6.7×10^{-5} to 7.7×10^{-5} m, were tested in order, with 7.2×10^{-5} m (0.7%) chosen as optimum (Fig. 3). The maximum $I_{100} - I_0$ value obtained (131.8) was lower than that obtained from the sensing membrane previously studied by us ($I_{100} - I_0 = 268.7$). The result obtained with amines seems to agree with their basicity. DBU responds better than the others because of its higher pK_a. The prepared membranes using DBU have a lifetime of about 20 days probably due to the loss of DBU by volatilization. On the basis of these results, we selected TMAOH as the transfer agent for the rest of the study, because the sensitivity is similar to other agents although the stability is better.

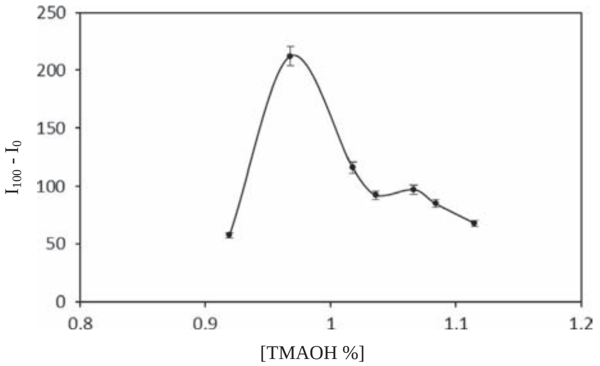

Fig. 2. Optimization of concentration of TMAOH in ethyl cellulose membrane.

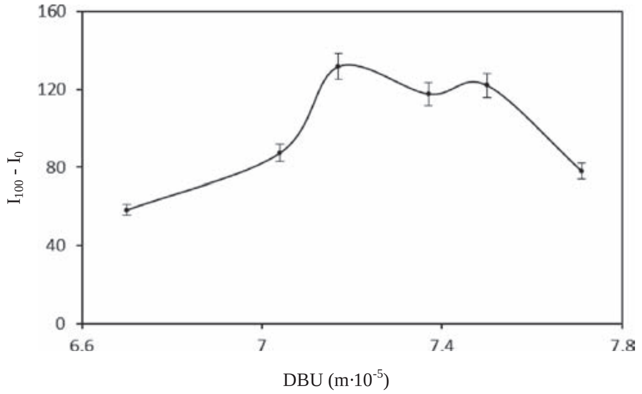

Fig. 3. Optimization of amount of DBU in membrane sensor B2.

The problem of loss of sensing membrane performance due to the loss of water was tackled by replacing the polymer membrane with a more hydrophilic one. Hydroxy propyl methylcellulose (HPMC) (Methocel E-5 Premium) is a forming membrane polymer with good permeability to gases and is flexible, transparent, water-soluble, and has moderate barriers to oxygen [40]. It is widely used as a coating material in various pharmaceuticals as well as foods [41], applications in which the prevention of oxidation and moisture loss from the product is required. It has also been used for gas permeation related to moisture sorption in films [42].

In order to solubilize HPMC to prepare cocktails containing α-naphtholphthalein, different solvents were tested (water, methanol, ethanol and dioxane), and water and dioxane were chosen. To optimize the amount of dioxane as the solvent, different percentages of HPMC between 55% and 75% in dioxane were tested. Membranes did not form if the percentage was higher or lower than this. The best result was obtained using 65% of HPMC in dioxane. The value of $I_{100} - I_0$ obtained was 124, a lower value than the reference value and for this reason its use for membrane making was discarded.

With water, the optimization was made preparing different cocktails containing 1 mL of water and different amounts of HPMC: 1%, 2%, 4% and 5%. 2% of HPMC in water turned out to be the minimum concentration required to form a membrane. In these conditions the membrane does not change at low CO_2 concentrations, and surfactants can be added [43], reducing the interfacial tension and facilitating the permeation of CO_2 gas.

We studied a group of surfactants originating from different types: 1) Mighty PSD, a copolymer polycarboxylate that is a polycarboxylate ether-based superplasticizer, is a polyacrilyc acid derivative with a high dispersing component; 2) Brig 35, a non-ionic polioxiethylene-type surfactant; 3) CTAB, a cationic- type surfactant; 4) Melflux 2651, a polycarboxilic ether; and 5) Tween 20, a non-ionic polyoxyethylene sorbitol ester. For each surfactant, different membranes were prepared, depending on the critical micellar concentration, in order to find the best composition of the cocktail. The amounts tested were: Mighty PSD (1–7 mg), Brij 35 (0.11–5 mg), CTAB (0.335–0.368 mg), Melflux 2651F (1–3.5 mg) and Tween 20 (1–75 mg), all of which were tested with varying percentages between 0% and 100% of CO_2.

Table 2 shows the results obtained for the best membrane of each type. Using Mighty PSD, Brij 35, CTAB and Melflux 2651F as surfactants, the sensing membranes exhibit poor sensibility to low concentrations of CO_2 along with a high response time. However, using Tween 20 as the surfactant, the response is fast in the entire concentration range studied, and was, thus, selected. Fig. 4 shows the influence of this surfactant on the response, with 0.06% w/w selected.

In the case of CO_2 sensor previously studied by us [25], cocktails A (acid–base indicator) and B (luminophore) were deposited on the opposite side of the transparent support because of different problems: resolubilisation of one membrane when we attempted to deposit one membrane on top of the other and the chemical reaction of PtOEP with TOAOH. However, in this case, as

Table 2
Optimization of membrane sensor B4 with different surfactants.

Parameter	Surfactant				
	Tween 20	Highty PSD	Brij 35	CTAB	Melflux 2651F
[Surfactant] optimum (% w/w)	0.06	0.70	0.50	0.04	0.25
$I_{100} - I_0$	280 ± 2	83.7 ± 0.7	120.8 ± 0.9	91.0 ± 0.6	87.2 ± 0.7
Slope	19.82 ± 0.01	23.212 ± 0.009	4.605 ± 0.007	3.041 ± 0.006	38.02 ± 0.09
Intercept	0.170 ± 0.005	0.35 ± 0.09	1.24 ± 0.09	0.83 ± 0.09	4.2 ± 0.1
R^2	0.994	0.991	0.992	0.994	0.951

the cocktail is made up in water, the membranes can be deposited one on top of the other, making a double-membrane configuration possible. In addition, the membrane does not acquire a dark colour because partial solubilization does not occur between the membranes. The advantage of this new arrangement over the previously-established one is that it is much simpler and allows for greater versatility and forms of subsequent inclusion in portable instrumentation.

3.1. Sensing membrane characterization

Using Eq. (1), a good fit in the whole range, derived from a threefold replica at room temperature (25 °C), is observed. The limit of detection (LOD) is obtained from exponential raw experimental data using the first three points at low CO_2 concentrations for each membrane because they can be adjusted to a straight line. The LODs were calculated as usual by $LOD = t_0 + 3s_0$, where t_0 is the average blank signal and s_0 is the critical level or standard deviation of the blank, which is determined from eight replicate measurements. The LODs found using this approach were: 0.007% CO_2 for sensor B1 and sensor B4, 0.034% for sensor B3 and 0.02% for sensor B2, equal to the value with the reference sensor, as observed in sensor type B3, which used dioxane to dissolve the polymer HPMC. The result is worse, however, with the B1-type sensor, using TMAOH with the polymer ethyl cellulose. Thus the B4-type sensor using water to dissolve the polymer HPMC performs better than the reference sensor. The limit of quantification (LOQ) [44] is obtained from the calibration function as

$$t_{LOQ} = t_0 - 10s_0 \qquad (2)$$

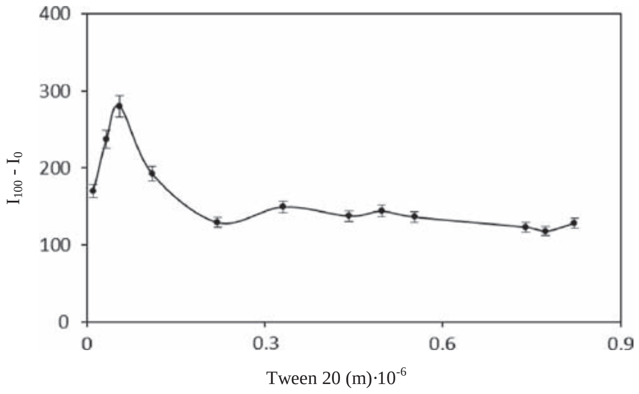

Fig. 4. Optimization of amount of Tween 20 in membrane sensor B4.

The results obtained are shown in Table 3 for all the sensors studied including the B2-type sensor. Although this sensor was discarded due to its poor results, we included it in the characterization for purposes of comparison; it could be seen that LOQ obtained in B2 and B3 sensors was worse than that in the reference sensor, while the B4 sensor was similar and the B1 was somewhat better than the reference sensor.

The precision in the measurement of CO_2 with the proposed sensing membranes was evaluated at two CO_2 concentrations (0.6% and 16.7%), performing 15 measurements each, and obtaining relative standard deviations. Table 3 shows the different analytical characteristics of the proposed membranes for CO_2, comparing the results with previously proposed sensor. The result in the case of comparing the precision at 0.6% CO_2 shows that B3-type sensors are worse than the reference sensor, the B2 sensor is similar to the reference sensor and for B1 and B4 sensors, the LOQs are similar and better than those of the reference sensor.

The result while comparing the precision at 16.7% CO_2 shows that B2 and B3 sensors are worse than the reference sensor, and for B1 and B4 sensors, the LOQs are similar to those of the reference sensor.

The sensor for carbon dioxide gas using TMAOH in ethyl cellulose as the phase transfer agent and polymer (B1) presents a value $I_{100} - I_0$, somewhat lower than that in the reference sensor, but better than the sensor proposed using DBU in ethyl cellulose (B2). The values found with the B1 sensor are similar to those of the reference sensor and with the B4 sensor they are slightly better than those of the reference sensor.

The response time for B2, B3 and B4 sensors was higher than that for the reference sensor. Only the B1 sensor produced better results than the reference sensor, about 20% lower. The recovery time for all the sensors tested was similar to the reference sensor. The dynamic response of the sensing membranes when exposed to alternating atmospheres of pure CO_2 and pure nitrogen was studied, with a response time between 10% and 90% of the maximum signal and a recovery time from 90% to 10% for all the membranes. In all cases, the signal changes were fully reversible and hysteresis was not observed during the measurements. Fig. 5 shows the result for the B4 sensor.

The stability – both short-term and long-term – of the sensing membranes is a very important issue for any real application. The long-term stability of luminophore membranes has been previously studied by us [25] for 210 days, with the sensor kept in darkness at room temperature and the phosphorescence measured periodically. A constant increase in the signal (about 60%) was observed until the ninth day, probably due to a curing process of the PVCD membrane containing PtOEP. Afterwards, the

Table 3
Characteristics of sensing membranes for CO_2 gaseous determination.

Analytical parameter	Membrane type				
	Ref.	Membrane B1	Membrane B2	Membrane B3	Membrane B4
$I_{100} - I_0$	269.0 ± 1.3	212.3 ± 1.5	131.7 ± 1.2	124.2 ± 0.9	280.0 ± 1.5
Slope	5.219 ± 0.007	0.50 ± 0.05	1.475 ± 0.009	5.37 ± 0.02	6.91 ± 0.04
Intercept	1.02 ± 0.09	0.9 ± 0.1	1.2 ± 0.1	0.8 ± 0.1	0. 55 ± 0.09
R^2	0.998	0.962	0.994	0.997	0.969
Measurement range (%)	0–100				
τ (days)	365	515	20	390	300
Precision (DER; $n = 15$) at 0.6% CO_2	0.56	0.345	0.590	0.6	0.335
Precision (DER; $n = 15$) at 16.7% CO_2	0.25	0.23	0.39	0.4	0.22
LOD (% CO_2)	0.02	0.007	0.02	0.034	0.007
LOQ (% CO_2)	5.9	3.1	14.6	11.1	5.1
Response time (t_{90}) (s)	9.3 ± 0.5	7.40 ± 0.04	24.1 ± 0.2	69.0 ± 0.7	41.0 ± 0.5
Recovery time (t_{10}) (s)	115 ± 2	113.0 ± 0.1	105.60 ± 0.03	113.0 ± 0.7	100 ± 2
Storage conditions	Humid atmosphere and in the dark	In the dark			

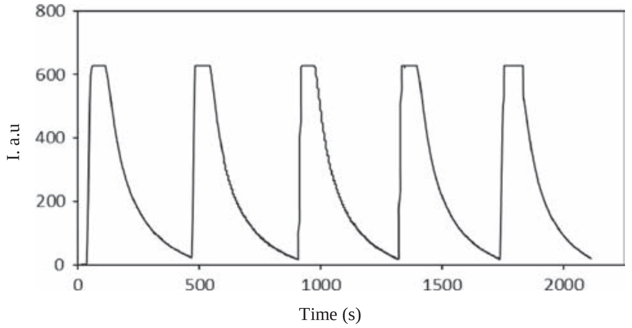

Fig. 5. Response and recovery characteristics of CO_2 sensing membrane while increasing and decreasing CO_2 concentrations (from 0% to 100% and vice versa) in membrane sensor B4.

phosphorescence decreased slowly by about 20% at the end of 210 days. The long-term stability of the indicator membrane, prepared from cocktail B1, was studied for 515 days, for the B4 sensor 300 days and for the B3 sensor 390 days, with no special conditions required except storage in darkness in all cases. In the case of B2 sensor, the lifetime was only 20 days without any special storage conditions, a result due to the high volatility of DBU.

4. Conclusions

An improvement has been observed for optical sensors for gaseous CO_2 based on the phosphorescence intensity measurement of the PtOEP complex included in PVCD membranes due to the displacement of the α-naphtholphthalein acid–base equilibrium. The use of TMAOH instead of TOAOH offers similar results in selectivity and precision but improves the stability and lifetime because it does not need to be held in a special atmosphere. The use of HPMC instead of ethyl cellulose offers similar results in selectivity and precision and also makes it unnecessary to preserve the membranes in special atmospheric conditions. In addition, replacing organic solvents with water in the preparation of cocktails is a greener way to prepare the sensors. Sensor B1 and B4 are more sensitive with a detection limit lower than in the reference sensor and a response time that is slightly higher than in the reference sensor, but with a similar recovery time. Thus, both offer a way to improve optical dry sensors in manner simplicity and with low cost for gaseous CO_2.

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