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Optical Carbon Dioxide Sensors Based on Silicone-Encapsulated Room-Temperature Ionic Liquids

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Novel optical carbon dioxide sensors are based on emulsion of room-temperature ionic liquids (RTILs)–1-butyl-3-methylimidazolium salts in a silicone matrix. Semiquantitative determination of CO_2 is achieved by dissolving an absorption-based pH indicator (thymol blue, TB, or bromthymol blue, BTB) in the RTIL. A quantitative fluorimetric sensor makes use of 8-hydroxypyrene-1,3,6-trisulfonate (HPTS). The response of the fluorimetric sensors to CO_2 can easily be linearized which makes (re)calibration of the sensor very simple. It is demonstrated that a reference inert fluorescent dye (4-dicyanomethylene-2-methyl-6-(4-(dimethylamino)styryl)-4*H*-pyrane) can be added for ratiometric measurements. It is also shown that stable inorganic salts such as sodium phosphate can be used instead of quaternary ammonium hydroxides. Sensitivity of the material can be tuned by varying the pK_a of an indicator. The sensors can find application in biotechnology, environmental monitoring, and food-packaging technology.

1. Introduction

Carbon dioxide is one of the most important compounds on earth. Produced by living beings, carbon dioxide is dangerous to them at high concentrations. The US Mine Safety and Health Administration, for example, has set the exposure limit for carbon dioxide at 0.5% for 8 h at underground and surface mines and a short-term exposure for underground coal mines at 3.0% for 15 min (at 1.5% for 15 min for metal and nonmetal mines). The US Occupational Safety and Health Administration considers concentrations exceeding 4% as "immediately dangerous to life and health". Apart from environmental monitoring,[1] a variety of other applications exist where knowing CO_2 concentration is essential. Measurement of CO_2 levels in blood[2,3] and seawater,[4–6] in respiratory analysis,[7] as well as gas level in greenhouses (where CO_2 content is raised to 1% to provide better plant growth and to eliminate pests) are among such applications. Knowing the concentration of dissolved CO_2 would also provide a better control over biotechnological processes.[8,9]

Modified atmosphere packaging (MAP) is a technique used to prolong the shelf-life period of fresh or minimally processed food.[10] In this method, the air surrounding the food in the package is changed to another gas composition. Very often high carbon dioxide levels (up to 100%) are desirable because surface growth of microorganisms is inhibited. Most optical sensors for CO_2 reported so far, however, exhibit too high sensitivity for this range of interest and become practically useless at concentrations of more than a few percent of CO_2.[5,7,11–14] It is not uncommon to make use of absorption-based pH indicators with high pK_a values to reduce sensitivity to carbon dioxide and thus enable measurements at higher p_{CO_2}.[15] It is however more difficult to design fluorescent sensors, since there are few fluorescent pH indicators which satisfy the requirements of pK_a, brightness, and photostability. A possible solution is a system using FRET from a luminescent inert dye to a nonfluorescent pH indicator.[16] von Bultzingslowen et al. have found that 8-hydroxypyrene-1,3,6-trisulfonate (HPTS) can be used for sensing high CO_2 levels if immobilized into an organically modified silica (ormosil) matrix.[17] In fact, the sensitivity of the system was much lower than for the same indicator used in plastic CO_2 sensors.[11] The sol–gel matrixes, however, are prone to aging caused by structural evolution of the sol–gel, which in turn severely can affect sensitivity to CO_2.[13]

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(1) Wolfbeis, O. S.; Kovacs, B.; Goswami, K.; Klainer, S. M. *Microchim. Acta* **1998**, *129*, 181.
(2) Meruva, R. K.; Meyerhoff, M. E. *Biosens. Bioelectron.* **1998**, *13*, 201.
(3) Cooney, C. G.; Towe, B. C.; Eyster, C. R. *Sens. Actuators B* **2000**, *69*, 183.
(4) Tabacco, M. B.; Uttamlal, M.; McAllister, M.; Walt, D. R. *Anal. Chem.* **1999**, *71*, 154.
(5) Neurauter, G.; Klimant, I.; Wolfbeis, O. S. *Fresenius J. Anal. Chem.* **2000**, *366*, 481.
(6) Montegut, C. G.; Begovic, M. *Deep-Sea Res., Part II* **2002**, *49*, 2049.
(7) Mills, A.; Lepre, A.; Wild, L. *Sens. Actuators B* **1997**, *38–39*, 419.
(8) Ferguson, J. A.; Healey, B. G.; Bronk, K. S.; Barnard, S. M.; Walt, D. R. *Anal. Chim. Acta* **1997**, *340*, 123.
(9) Ge, X.; Kostov, Y.; Rao, G. *Biotechnol. Bioeng.* **2005**, *89*, 329.
(10) Church, N. *Trends Food Sci. Technol.* **1994**, *5*, 345.
(11) Mills, A.; Chang, Q. *Analyst* **1993**, *118*, 839.
(12) Mills, A.; Chang, Q.; McMurray, N. *Anal. Chem.* **1992**, *64*, 1383.
(13) Nivens, D. A.; Schiza, M. V.; Angel, S. M. *Talanta* **2002**, *58*, 543.
(14) Mills, A.; Chang, Q. *Sens. Actuators B* **1994**, *21*, 83.
(15) Mills, A.; Chang, Q. *Anal. Chim. Acta* **1994**, *285*, 113.
(16) von Bultzingslowen, C.; McEvoy, A. K.; McDonagh, C.; MacCraith, B. D. *Anal. Chim. Acta* **2003**, *480*, 275.
(17) von Bultzingslowen, C.; McEvoy, A. K.; McDonagh, C.; MacCraith, B. D.; Klimant, I.; Krause, Ch.; Wolfbeis, O. S. *Analyst* **2002**, *127*, 1478.

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Although this inconvenience may be overcome by allowing the sensor material to age for several weeks,[17] development of alternative materials is still of much interest.

In this work, we report novel carbon dioxide-sensitive materials which make use of an emulsion of a room-temperature ionic liquid in a silicone matrix. We demonstrate that the sensitivity of the sensors can be tuned by varying the pK_a of an indicator used. When using pH indicators with relatively low pK_a (~7–8 in aqueous medium) the materials still exhibit lower sensitivity than most CO_2 sensors and thus are suitable for sensing of higher CO_2 levels.

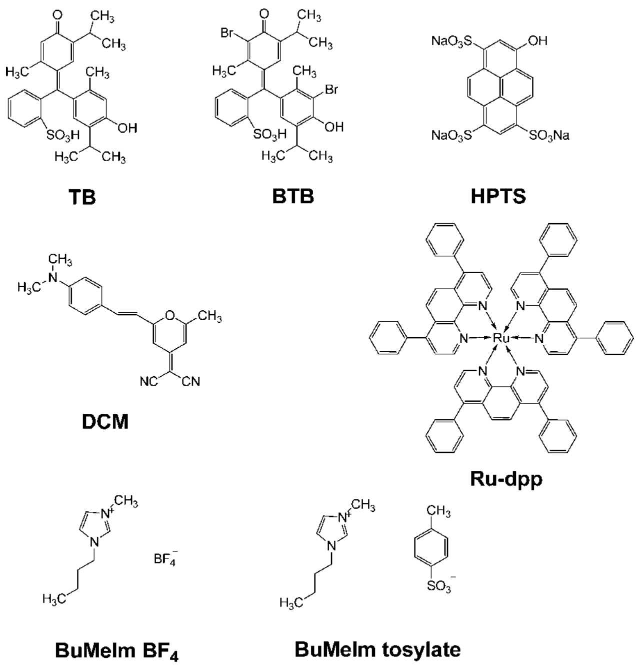
2. Experimental Section

Materials. Thymol blue (TB), bromthymol blue (BTB), 4-dicyanomethylene-2-methyl-6-(4-(dimethylamino)styryl)-4*H*-pyrane (DCM), titanium(IV) oxide powder, and tetrabutylammonium hydroxide (TBAOH) solution in water (40 wt %) were obtained from Aldrich. Sodium hydrocarbonate and sodium phosphate dodecahydrate from Merck, 1-butyl-3-methylimidazolium tetrafluoroborate ($BuMeImBF_4$) and 1-butyl-3-methylimidazolium tosylate (BuMeIm tosylate), vinyl-terminated polydimethylsiloxane (PDMS) (DMS-V33, viscosity 3500 cSt), methylhydrosiloxane/dimethylsiloxane copolymer (HMS-301), tetravinyltetramethylcyclotetrasiloxane (SIT 7900.0), and platinum divinyltetramethylsiloxane complex (PC075) from ABCR, trisodium 8-hydroxypyrene-1,3,6-trisulfonate (HPTS) from Fluka, and poly(ethylene glycol terephthalate) support Mylar from Goodfellow were used as received. Nitrogen, oxygen and carbon dioxide, all of 99.999% purity, were obtained from Linde. The inert luminescent reference particles were prepared analogously to the literature procedure[18] from ruthenium(II) tris(4,7-diphenyl-1,10-phenanthroline) dichloride (= Ru-dpp) and polyacrylonitrile.

The chemical structures of the indicators, reference substances, and ionic liquids are presented in Chart 1.

Preparation of the Absorption-Based and Fluorescent Sensing Materials. The buffer system was prepared in the following manner. Four milligrams of an indicator (TB or BTB) was dissolved in the mixture of 15 μL of TBAOH aqueous solution and 15 μL of doubly distilled water. Alternatively, 4 mg of HPTS was dissolved in 30 μL of 0.2 M solution of sodium hydrocarbonate or sodium phosphate. 200 μL of the RTIL was mixed thoroughly for 1 h with the solution of an indicator. The cocktail of silicone primers was obtained by mixing tetravinyltetramethylcyclotetrasiloxane (1.5 μL) with 500 mg of the vinyl-terminated PDMS followed by addition of 15 μL of methylhydrosiloxane–dimethylsiloxane copolymer and 2 μL of the platinum complex catalyst. The emulsion was prepared by adding of 50 μL of the buffer system to the silicone composition and mechanically stirring the mixture at 1500 rpm for 1 min. The emulsion was vacuumized to remove air bubbles, mixed, vacuumized once again, and knife-coated (using a K Control Coater) onto a dust-free polyester support. The thickness of the sensing layer was 60 μm. The curing process was complete within 10 min at 50 °C. The sensor foils were coated with a 60 μm light-reflecting layer to achieve better visual effects in case of absorption-based sensors and higher signal amplitude for the fluorescent sensors. The cocktail prepared from 30 mg of TiO_2 powder and 518 mg of silicone primers composition was spread and cured in the manner described above.

Chart 1. Chemical Formulas of the Indicators, Reference Substances, and RTILs



TB **BTB** **HPTS** **DCM** **Ru-dpp** **BuMeIm BF$_4$** **BuMeIm tosylate**

Table 1. Composition of the CO_2 Sensor Materials

sensor material	RTIL	indicator	base
SM-1	$BuMeImBF_4$	HPTS	$NaHCO_3$
SM-2	$BuMeImBF_4$	HPTS	Na_3PO_4
SM-3	BuMeIm tosylate	HPTS	$NaHCO_3$
SM-4	$BuMeImBF_4$	TB	TBAOH
SM-5	$BuMeImBF_4$	BTB	TBAOH

Preparation of the DLR-Sensor Material. The above procedure was modified so that 20 mg of the reference luminescent microbeads was dispersed in 518 mg of the silicone primers mixture, the sensor prepared further as described above.

Preparation of the Ratiometric Sensor Material. One milligram of 4-dicyanomethylene-2-methyl-6-(4-(dimethylamino)styryl)-4*H*-pyrane (DCM) was predissolved in 100 μL of acetone, and 200 μL of the RTIL was added. Nitrogen was bubbled through the solution until all acetone was removed. Then, 30 μL of a 0.2 M aqueous solution of sodium phosphate was added. The sensing material was prepared by subsequently mixing 20 μL of the HPTS buffer solution (dissolved in the RTIL containing sodium phosphate) and 5 μL of the DCM buffer solution into 518 mg of the uncured silicone composition. The cocktail was spread and cured in the manner described above. The composition of the sensor materials is summarized in Table 1.

Measurements. Absorption and emission spectra were recorded respectively on a Lambda 14 p UV–vis spectrophotometer and an Aminco AB 2 luminescence spectrometer. The response of the sensor was measured using a two-phase lock-in amplifier (SR830, Standford Research Inc. A sensor film was placed in a homemade flow-through cell and excited with the sinusoidally modulated (at 45 kHz) light of a blue LED (λ_{max} = 470 nm, Yoldal). The excitation light was filtered through an interference filter of type FITCA (Schott). Luminescence filtered through a long-pass filter OG 530 (Schott) was detected with a photomultiplier tube (type H5701-02, from Hamamatsu). The response of the ratiometric sensor was characterized using two interference band-pass filters: FITCE (Schott) for HPTS emission and Chroma 650/60 (AHF Analysentechnik) for DCM emission. A bifurcated fiber bundle was

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[18] Borisov, S. M.; Vasylevska, G. S.; Krause, Ch.; Wolfbeis, O. S. *Adv. Funct. Mater.* **2006**, *11*, 1536.

used to guide the excitation light to the sensor foil and to guide back the luminescence.

Dynamic response to varying concentrations of CO_2 and sensor photostability were studied using a pH-mini detection device (Presens GmbH) which analogously to the above setup uses a 470-nm LED excitation and a similar set of the excitation and emission filters.

Temperature was controlled by a Lauda RC6 cryostat (Lauda). Gas calibration mixtures were obtained using a gas mixing device (MKS, Wilmington). In order to humidify the test gases, the respective gas mixtures were bubbled through water so that 100% relative humidity was achieved. Photographic images of the sensor foil were acquired using a Canon 350D digital camera. Microscopic images of the sensor foils were acquired using a color Leica DC 200 digital camera mounted onto a Leica DMRE microscope.

3. Results and Discussion

Composition of the Sensors. The variety of sensors reported for optical sensing of carbon dioxide can be divided into two large groups: the sensors based on the Severinghaus technique[19] and those using plastic films.[12] In the first sensor type the sensing chemistry occurs in a bicarbonate buffer solution (where a pH indicator is dissolved), which is separated from the analyzed gas or liquid medium by a gas-permeable membrane.[4,20,21] While more stable over time and less sensitive to highly acidic gases, the manufacture of such sensors is rather complicated. Plastic solid state sensor films,[22] on the other hand, are easy to manufacture. They contain a pH indicator and a lipophilic organic base which are dissolved in a hydrophobic polymer.[5,9,12,23–26] The sensitivity of such materials is, however, often too high for application in the food packaging technology.

The novel carbon dioxide sensor material presented here is based on an emulsion of a room-temperature ionic liquid (RTIL) in a silicone matrix. Although the emulsion-based materials were reported previously for optical sensing of ammonia[27] and carbon dioxide,[28,29] they relied on aqueous solutions of the indicators. Such systems, however, are not fairly reproducible because once dehydrated it is difficult for the sensor to return to the initial state. We perceived that RTILs can be an excellent alternative to the aqueous emulsion. RTILs benefit from negligible vapor pressure, excellent thermal stability, and low toxicity and are used increasingly often in various fields of science and technology. RTILs possess excellent solubility for carbon dioxide,[30–33] which makes them particularly attractive for CO_2 sensing. Although the feasibility of using RTILs for detection of CO_2 in solution was demonstrated,[34,35] such a system has severe practical limitations.

The buffer system is based on 1-butyl-3-methylimidazolium tetrafluoroborate, which was chosen as a model RTIL. Apart from the dissolved indicator, the buffer also includes water (15 vol %) and a base (organic or inorganic). We used both absorption-based (TB and BTB) and a fluorescent pH indicator (HPTS) to demonstrate the feasibility of the approach. Tetrabutylammonium hydroxide was used as a base together with TB and BTB. It was found, however, that quaternary ammonium hydroxides are not suitable for use along with HPTS. The ion pair formed between the negatively charged indicator and the positively charged quaternary ammonium ions [e.g., $HPTS(TBA)_3$] becomes too lipophilic to be soluble in the polar RTIL. Indeed, we observed even less solubility of the ion pair when using a more lipophilic tetraoctylammonium hydroxide. The fact is not surprising because quaternary ammonium salts are commonly used to transform hydrophilic HPTS anion into a lipophilic ion pair, which is highly soluble in apolar solvents and polymer matrixes such as ethylcellulose[5,11,26,36] and silicone.[9,37,38] Thus, stable inorganic salts such as sodium hydrocarbonate and sodium phosphate were employed together with HPTS. In contrast to the plastic sensors, where a lipophilic polymer-soluble base is a must, virtually any inorganic salt that produces hydroxide ions upon hydrolysis can be used in our system. It should be noted that either $NaHCO_3$, Na_2CO_3, or NaOH can be used and give identical performance since the equilibrium between HCO_3^- and CO_2 is established as soon as carbon dioxide is present in the system.

To obtain an emulsion-based optical sensor the buffer system should be entrapped in a gas permeable *polymer matrix*. We prefer to use polydimethylsiloxane-based silicones for this purpose because they possess excellent permeability (P) for carbon dioxide ($P = 3.49 \times 10^{-10}$ cm^2 s^{-1} Pa compared to 8.48×10^{-12} cm^2 s^{-1} Pa for ethylcellulose and 7.9×10^{-13} cm^2 s^{-1} Pa for polystyrene)[39] and water vapor but are impermeable to polar ionic species. The latter property also is of a much importance for the sensor material because the buffer components cannot dissolve in the polymer matrix. The two-component addition-cure silicone used here is particularly attractive for this application because it does not require a solvent and produces no acidic or basic substances upon curing (such as acetic acid or amine curing silicones). Moreover, the viscosity of the polymer cocktail can be easily varied. When using microbeads, lower viscosity is preferred (which is achieved by using polydimethylsiloxanes having lower molecular mass).[26] For a stable

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(19) Severinghaus, J. W.; Bradley, A. F. *J. Appl. Physiol.* **1958**, *13*, 515.
(20) Zhujun, Z.; Seitz, W. R. *Anal. Chim. Acta* **1984**, *160*, 305.
(21) He, X.; Rechnitz, G. A. *Anal. Chem.* **1995**, *67*, 2264.
(22) Raemer, D. B.; Walt, D. R.; Munkholm, C. US Patent 5.005.572, 1991.
(23) Weigl, B. H.; Wolfbeis, O. S. *Sens. Actuators B* **1995**, *28*, 151.
(24) Nakamura, N.; Amao, Y. *Sens. Actuators B* **2003**, *92*, 98.
(25) von Bültzingslöwen, C.; McEvoy, A. K.; McDonagh, C.; MacCraith, B. D. *Anal. Chim. Acta* **2003**, *480*, 275.
(26) Borisov, S. M.; Krause, Ch.; Arain, S.; Wolfbeis, O. S. *Adv. Mater.* **2006**, *18*, 1511.
(27) Wolfbeis, O. S.; Posch, H. E. *Anal. Chim. Acta* **1986**, *185*, 321.
(28) Hui, H. K.; Bankert, C. S. Eur. Pat. Appl. EP 1990-308694.0, 1990.
(29) Parker, J. W.; Laksin, O.; Yu, C.; Lau, M. L.; Klima, S.; Fisher, R.; Scott, I.; Atwater, B. W. *Anal. Chem.* **1993**, *65*, 2329.
(30) Scovazzo, P.; Camper, D.; Kief, J.; Poshusta, J.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *13*, 6855.
(31) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049–3054.
(32) Lee, B. C.; Outcalt, S. L. *J. Chem. Eng. Data* **2006**, *51*, 892.
(33) Jacquemin, J.; Costa Gomes, M. F.; Husson, P.; Majer, V. *J. Chem. Thermodyn.* **2006**, *38*, 490.
(34) Oter, O.; Ertekin, K.; Topkaya, D.; Alp, S. *Sens. Actuators B* **2006**, *117*, 295.
(35) Oter, O.; Ertekin, K.; Topkaya, D.; Alp, S. *Anal. Bioanal. Chem.* **2006**, *386*, 1225.
(36) Weigl, B. H.; Wolfbeis, O. S. *Sens. Actuators* **1995**, *28*, 151.
(37) Werner, T.; Klimant, I.; Wolfbeis, O. S. *Analyst* **1995**, *120*, 1627.
(38) Mohr, G. J.; Werner, T.; Oehme, I.; Preininger, C.; Klimant, I.; Kovacs, B.; Wolfbeis, O. S. *Adv. Mater.* **1997**, *9*, 1108.
(39) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Grulke E. A., Eds.; John Wiley & Sons: New York, 1999.

emulsion it is, however, desirable to have a more viscous cocktail. Thus, a vinyl-terminated PDMS with viscosity of 3500 cSt was used as the main component. A stable emulsion is easily obtained after several seconds of mixing (at a speed of 1500 rpm). The sensor "cocktail" obtained by mixing the buffer system into the uncured silicone was spread onto the transparent polyester foil and cured at 50 °C for 10 min to give a sensor layer in a thickness of ~60 μm. When preparing absorption-based sensors, a light-reflecting layer (TiO_2 in silicone) was spread over the sensor layer to achieve better visual effects.

The sensing scheme is straightforward. Carbon dioxide diffuses through the silicone and dissolves in the buffer system where it reversibly reacts with a base. At higher CO_2 concentrations pH is thus reduced and the indicator becomes protonated, which is monitored visually or specrtoscopically (via absorbance or fluorescence).

Although fluorescence intensity is a classical parameter, it suffers from drifts of the optoelectronic system, photobleaching, and variation in the optical properties of the sample such as turbidity, coloration, and refractive index. Therefore, several sensor materials were investigated which made use of self-referencing techniques. The intensity of fluorescence is not measured as an independent magnitude by itself but is referenced against the luminescence intensity (or decay time) of a second inert and spectrally compatible luminophore. Dual excitation of HPTS (at ~470 and 405 nm) enables self-referencing,[13,40] which, however, can only be achieved by using a fluorometer-like setup (one excitation source combined with a set of excitation filters or a monochromator). Since excitation with the LEDs is more suitable for practical purposes, we investigated the feasibility of the dual lifetime referencing (DLR) method[41,42] and ratiometric intensity measurements. A DLR sensor was prepared by dispersing inert reference microbeads (Ru-dpp in PAN) in the silicone along with the CO_2-sensitive buffer. A ratiometric sensor made use of the reference fluorescent dye DCM. Here, the solution of the dye in the RTIL-based buffer system was additionally dispersed in the silicone.

The sensor films were investigated with help of fluorescent microscopy to establish the morphology of the material. Figure 1 (upper part) shows a microscopic image of the sensor material SM-3. Evidently no droplets are distinguishable, and the canal-like porous structure is formed. Such a structure does not significantly influence the mechanical properties of the material; however, the swelling properties are affected as will be shown later.

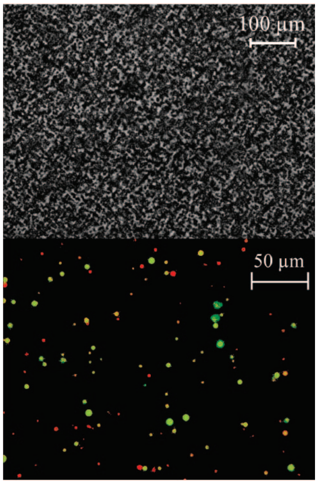

Figure 1. Microscopic images of the sensor materials. Upper part: absorption image of SM-3. Lower part: fluorescence image of the ratiometric sensor material upon excitation with blue light. In both cases the thickness of the foil is ~14 μm.

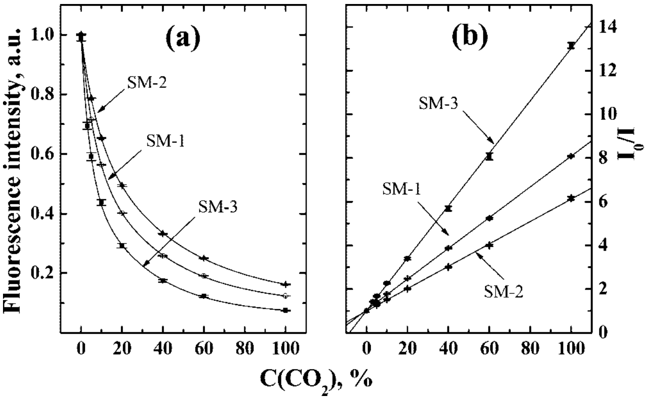

Figure 2. Response of the fluorescent sensing materials to carbon dioxide.

If the amount of emulsion is reduced significantly compared to the amount in the sensor materials (9% w/w), the individual droplets become distinguishable. As an example, Figure 1 (lower part) shows the fluorescence image of the ratiometric sensor foil with reduced emulsion content (by 10-fold here). Upon excitation with blue light ($\lambda_{max} = 470$ nm) green fluorescence of HPTS and red fluorescence of the reference dye DCM are visible. The size of the droplets varies from 2.5 to 12.5 μm.

Fluorescent Optical Sensors. The response of the sensors to carbon dioxide is shown in Figure 2a. The response curve can easily be linearized in coordinates I_0/I vs $C(CO_2)$, where I_0 is the fluorescence intensity in the absence of carbon dioxide. As was shown by He and Rechnitz,[21] the response of a fluorescent pH indicator in the aqueous bicarbonate buffer system can be described by a Stern–Volmer-like equation:

$$\frac{I_0}{I} = 1 + KC(CO_2) = 1 + \frac{K_1\alpha}{K_{Ind}N}\, C(CO_2) \qquad (1)$$

where $K = K_1\alpha/K_{Ind}N$, K_1 is the first dissociation constant of carbonic acid, K_{Ind} is the dissociation constant of the pH indicator, N is the concentration of the bicarbonate ion in the buffer solution, and α is the proportionality constant between the external carbon dioxide concentration and concentration of the dissolved CO_2. Similar linear behavior was shown to be common for the plastic CO_2 sensors as well.[11,14,43]

As can be seen from Figure 2b, eq 1 indeed describes experimental data very well (with the correlation coefficient

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(40) Kermis, H. R.; Kostov, Y.; Harms, P.; Rao, G. *Biotechnol. Prog.* **2002**, *18*, 1047.

(41) Klimant, I.; Huber, Ch.; Liebsch, G.; Neurauter, G.; Stangelmayer, A.; Wolfbeis, O. S. In *Springer Series in Fluorescence Spectroscopy*; Valeur, B., Brochon, J. C., Eds.; Springer: Berlin, 2001; Vol. 1, p 257.

(42) Huber, Ch.; Klimant, I.; Krause, Ch.; Wolfbeis, O. S. *Anal. Chem.* **2001**, *73*, 2097.

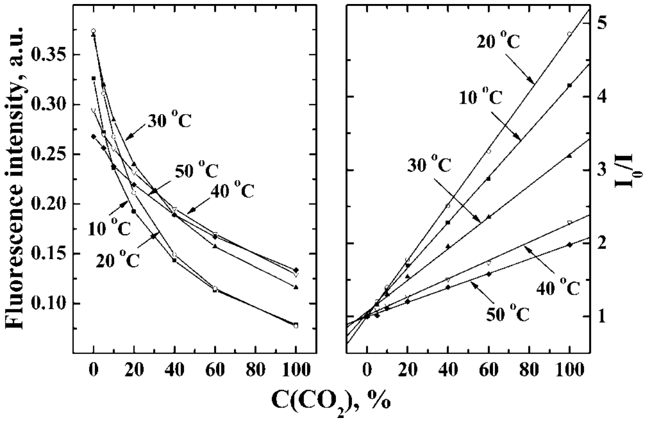

Figure 3. Temperature dependence of the response of the SM-1 to carbon dioxide.

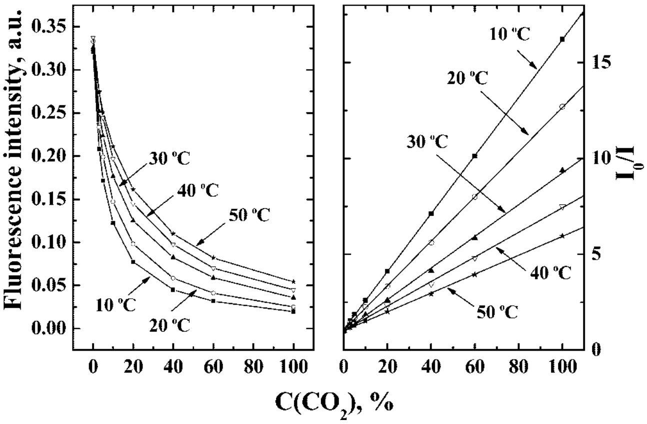

Figure 4. Temperature dependence of the response of the SM-3 to carbon dioxide.

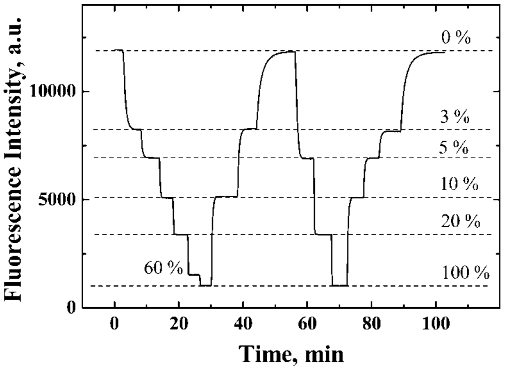

Figure 5. Response of the sensor material SM-3 to altering concentration of carbon dioxide.

$r^2 > 0.997$). The behaviors of an indicator in the RTIL-based system and in the aqueous buffer solution are thus very similar. Once the calibration plots are obtained, recalibration of the sensor can be performed if necessary (e.g., after continuous use resulting in photobleaching).

The sensitivity of the material can be tuned by using different base components in the buffer system. It was found out that sodium phosphate can also be used, and the resulting sensor material (SM-2) shows lower sensitivity than the material based on sodium hydrocarbonate (Figure 2). Moreover, the sensitivity of the system to CO_2 also is governed by the nature of counterion in the RTIL. In fact, the material which makes use of tosylate salts of 1-butyl-3-methylimidazolium (SM-3) shows significantly higher response to CO_2 compared to the materials based on 1-butyl-3-methylimidazolium tetrafluoroborate (Figure 2). In fact, the K values were calculated to be 0.070, 0.051, and 0.120 respectively for SM-1, SM-2, and SM-3. The materials based on tosylate salts exhibit sufficient dynamic in the range from 0 to 20% CO_2 ($I_0/I = 3.4$ for SM-3) and therefore can also be potentially applied in biotechnology and for clinical diagnostic purposes. The reason for significantly higher sensitivity of the tosylate-based material to CO_2 is likely to be better solubility of carbon dioxide in the ionic liquid composed of a more bulky anion. Certain substituents in the cation (such as longer alkyl chains) can potentially further tune the sensitivity. These RTILs, unfortunately, are not commercially available.

It is known that the sensitivity of optical CO_2 sensors is highly temperature dependent.[12,44,45] Since temperature can vary in many practical applications, it should be determined in an independent measurement in order to calculate correctly the concentration of carbon dioxide. We have therefore investigated the temperature dependence of the CO_2-sensitive materials. It was found that the sensor materials based on tetrafluoroborate salts of 1-butyl-3-methylimidazolium did not show stable performance at varying temperatures (Figure 3). The sensor materials SM-1 and SM-2 exhibited varying fluorescence intensity in the absence of carbon dioxide I_0 which was the highest at 20–30 °C. Although the sensor materials SM-1 and SM-2 behave reproducibly at room temperature (in the interval from 20 to 30 °C I_0 remains constant), their performance is compromised at higher and lower temperatures. We assume that such effects can be caused by low solubility of the components (indicator and base) in the RTIL at low and high temperatures. The sensor materials SM-1 and SM-2 are thus hardly suitable for real-world applications (including food-packaging technology) since variation of ambient temperature as well as sensor storage at varying temperatures will result in poorer reproducibility.

In contrast to the materials based on $BuMeImBF_4$, the sensor material SM-3 shows fully reproducible behavior at temperatures from 10 to 50 °C (Figure 4). The I_0 remains constant, while the sensitivity decreases at higher temperatures. Such behavior is common for all optical carbon dioxide sensors, including plastic sensors. Polar sulfo groups in tosylate anion are likely to favor solubility of the ionic species while its aromatic character can further help to solubilize HPTS. It is evident that, despite the reproducible temperature dependence, if the measurements are performed at varying temperatures, the latter should be determined in an independent measurement so that the temperature effects could be compensated for.

Reproducibility and Response Times. As can be seen from Figure 5, the sensor material SM-3 responds fully reproducible to carbon dioxide. The response times t_{95} were

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(43) Neurauter, G.; Klimant, I.; Wolfbeis, O. S. *Anal. Chim. Acta* **1999**, *382*, 67.

(44) Borisov, S. M.; Neurauter, G.; Schroeder, C.; Klimant, I.; Wolfbeis, O. S. *Appl. Spectrosc.* **2006**, *60*, 1167.

(45) Mills, A.; Lepre, A. *Analyst* **1999**, *124*, 685.

estimated to be 50 s on going from 0 to 100% CO_2 and 320 s in the reverse direction.

Photostability and Long-Term Stability. Photostability of the sensor material SM-3 was estimated using a phase detection device that makes use of a 470 nm LED as an excitation source. Under pure nitrogen we observed a 2.5% degradation of fluorescence intensity per every 1000 data points. A similar decrease (3.3%) was observed under 100% CO_2. It should be mentioned, however, that the actual rate of photobleaching is lower because only a minor fraction of the indicator is excited (deprotonated form) and photobleaches. As expected, photodecomposition was significantly higher in the presence of oxygen. In synthetic air (80% N_2 and 20% O_2) it was 8.3% per 1000 data points. Again, photobleaching should be less significant when some carbon dioxide is present. Much faster photodegradation rates under air saturation can thus be a serious problem when long-time measurements are performed.

The sensor materials can be stored at room temperature in a desiccator under 100% relative humidity and 10% CO_2 for a period of 1 month without alteration in sensor properties. If stored under 0% humidity, a substantial time of several hours is needed for the materials SM-1 and SM-2 to hydrate and become sensitive. The sensor material SM-3 still retains a substantial amount of water even in this condition, and only 10–30 min in humidified air is required to reach stable behavior. Notably, the sensor material SM-3 still responds to carbon dioxide at relative humidities close to 0 and shows sensitivity similar to that in humidified gas. Absolute intensity values were found to be ~10% lower in humidified gas which is likely to be caused by swelling of the film in these conditions.

Measurements in Aqueous Solutions. When measurements are performed in aqueous media for a prolonged period of time (tens of hours), a significant decrease in the luminescence intensity is observed. The mechanical properties of the material were altered as well, indicating significant swelling. The swelling of the material was confirmed in the following experiment (Figure 6). Droplets of water were placed onto the sensor foil which was then stored in a desiccator under 100% relative humidity for a period of 10 days. The sensor layer was destroyed by swelling in the places which contacted with water droplets (Figure 6). Moreover, the indicator was extracted to the aqueous phase which became colored. Evidently, the porous structure of the material is responsible for swelling.

The long-term stability of the sensor materials in aqueous media can be substantially improved if the sensor layer is coated with an inert ~60 μm thick silicone layer. No swelling of the sensor foil was observed after 10 days. It should be noted that the problem can not be tackled completely in this way since sensor spots (which are cut from the sensor foils) should be coated with the protective layer from the sides as well.

Referencing of Fluorescence Intensity. The dual lifetime referencing (DLR) method relies on simultaneous excitation of fluorescent indicator and luminescent reference dye and measuring the overall phase shift. The dye used for referencing purposes ideally should remain inert and should not exhibit any quenching by oxygen and other species. Thus, the dye is entrapped in oxygen-impermeable matrix, mostly polyacrylonitrile and the like, and used in the format of micro- or nanobeads. The beads can easily be dispersed in the polymer matrix together with the sensing droplets. Unfortunately, we observed that simultaneous mixing of *nano*beads into the emulsion resulted in formation of large aggregates which also severely affected the mechanical properties of the sensor layer. The sensor materials were obtained when using *micro*beads, but pronounced cross-sensitivity to oxygen appeared. Since the microbeads alone are not oxygen-sensitive, we assume they tend to hydrolyze when in contact with the emulsion.

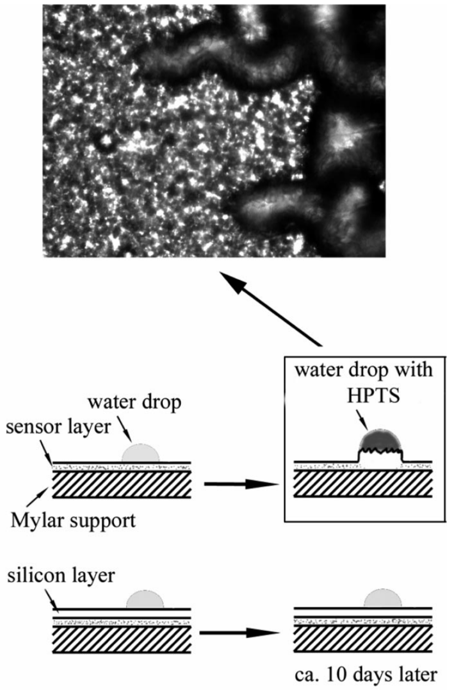

Figure 6. Schematic representation of the swelling experiment and the microscopic image of the droplet region of the sensor foil (SM-3) obtained after a period of 10 days.

The feasibility of ratiometric intensity measurements also was investigated. The ratiometric sensor material made use of the reference fluorescent dye DCM, which is excited together with HPTS by the light of a 470 nm LED but emits in the red part of the spectrum (Figure 7). The material contained droplets of two kinds: the CO_2-sensitive ones of the same composition as in SM-2 and the referenced droplets containing DCM dissolved in the RTIL. The emission of material in two optical windows (515–565 nm, isolated with a FITCE interference filter, and 620–680 nm, isolated with a Chroma 650/60 interference filter) was monitored. The response of the sensor is shown in Figure 8. Surprisingly, the fluorescence intensity of DCM also decreased (by ~2-fold) when elevating CO_2 content from 0 to 100%, which can be originated from changes in polarity of the medium. Since the emission spectrum of HPTS and the absorption spectrum of DCM overlap, another reason for the observed phenomenon can be energy transfer from HPTS to DCM. This results in the increased fluorescence intensity of DCM in the absence of CO_2. Despite this complication, the plots

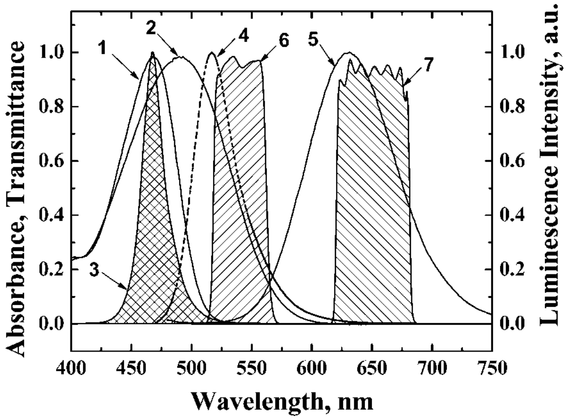

Figure 7. Spectral properties of the dyes used in the ratiometric sensor material, the excitation source, and optical filters: 1 and 2, absorption spectra of HPTS and DCM, respectively; 3, 4, and 5, emission spectra of the 470 nm blue LED, HPTS, and DCM, respectively; 6 and 7, transmittance spectra of the optical filters FITCE and Chroma 650/60.

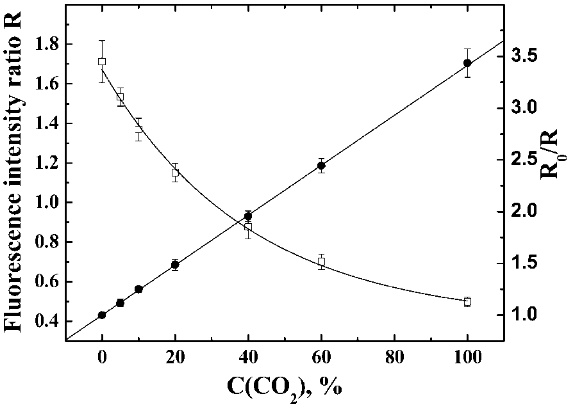

Figure 8. Calibration plot for the sensor material SM-2 containing DCM emulsion for reference purposes. R_0 and R are respectively the ratios of fluorescence intensities (I_{HPTS}/I_{DCM}) in the absence and in the presence of carbon dioxide.

of R_0/R vs $C(O_2)$ (where R_0 is the ratio of fluorescence intensities in the absence of carbon dioxide) were found to be linear (Figure 8).

Absorption-Based Sensor Materials. The sensor materials SM-4 and SM-5 make use of the indicators thymol blue and bromthymol blue, respectively, which have similar composition and spectral properties but significantly different pK_a values (9.2 and 7.3 for TB and BTB in aqueous solution).[46] The pK_a values of both, however, are in the range that is potentially useful for carbon dioxide sensing. Even though all absorption-based sensors can be used for quantitative determination of CO_2 (via absorption or reflection), first of all they are best suited for semi-quantitative determination of the analyte. The indicators TB and BTB, therefore, also satisfy best the requirement of a distinct color change in the presence of carbon dioxide (Figure 9). Indeed, the color of both changes from blue in the basic media to yellow in the acidic. Media having intermediate pH (close to the equivalence point) can also be distinguished (green color). Other absorption-based pH indicators such as phenol red, cresol red, *m*-cresol purple, neutral red, and naphtholphthalein can also be potentially useful but were rejected because of their less favorable spectral properties.

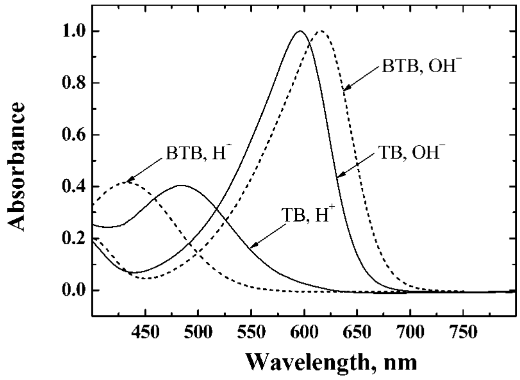

Figure 9. Absorption spectra of the indicators thymol blue (TB) and bromthymol blue (BTB) in aqueous solution.

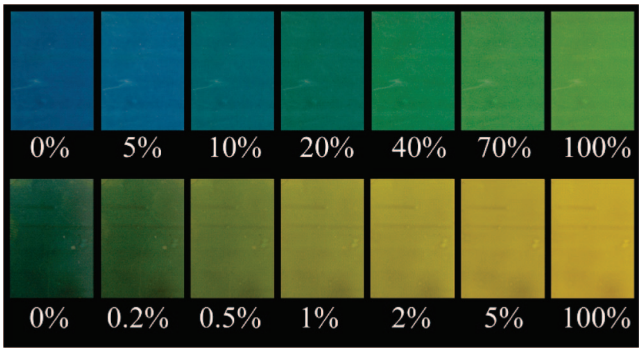

Figure 10. Photographic images of the sensor foils SM-5 (upper row) and SM-4 (lower row) at varying of carbon dioxide content in gas (20 °C, 100% relative humidity, normal barometric pressure).

Photographic images of the sensor foils based on BTB and TB at varying concentrations of carbon dioxide are shown at Figure 10. It is evident that the sensitivity of the system is determined by the pK_a of an indicator used. The sensor based on BTB, which has a lower pK_a, is sensitive to carbon dioxide in the dynamic range from 0 to 100%, which results in color change from dark blue to yellowish-green. The sensor thus can be suitable for application in the food-packaging technology. The sensor based on TB is much more sensitive. Because of the high pK_a of the indicator, it is not likely to be deprotonated completely even in the absence of CO_2. The visual effects are observed in the dynamic range from 0 to 2% CO_2, the sensor being practically insensitive at higher concentrations of the analyte. Such more sensitive sensors, however, can be suitable for CO_2 monitoring in closed areas where carbon dioxide is used or stored and in the closed poor ventilated working areas.

4. Conclusion

We have developed novel materials for carbon dioxide sensing and imaging which make use of the emulsion of RTIL in silicone matrix. Absorption-based and fluorescent materials allow (semi)quantitative determination of the analyte in gas phase. The sensitivity of the materials to CO_2 is determined by several factors: (a) the pK_a of an indicator, (b) the nature of counterion in the RTIL, and

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[46] Bishop, E. *Indicators*; Pergamon Press: New York, 1972.

(c) the nature of base used in the buffer. All the sensing materials exhibit excellent linearity of the calibration plots. The novel materials show good long-term stability but only moderate photostability. When used for measurements in aqueous environment, the sensor deteriorates quickly unless a protective silicon layer is applied. Referenced ratiometric measurements also are demonstrated. The fluorescent materials based on 1-butyl-3-methylimidazolium tetrafluoroborate suffer from irreproducible temperature dependence and therefore are hardly suitable for real-world applications. The material based on the tosylate salt can be potentially applied for clinical diagnostic purposes, environmental monitoring, biotechnological applications, and in food-packaging technology.

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