Direct Optical Carbon Dioxide Sensing Based on a Polymeric Film Doped with a Selective Molecular Tweezer-Type Ionophore

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Direct Optical Carbon Dioxide Sensing Based on a Polymeric Film Doped with a Selective Molecular Tweezer-Type Ionophore

Xiaojiang Xie, Marcin Pawlak, Mary-Lou Tercier-Waeber, and Eric Bakker*

Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Quai Ernest-Ansermet 30, CH-1211 Geneva, Switzerland

Ⓢ Supporting Information

ABSTRACT: A novel optical method for the determination of CO_2 concentration in aqueous and gaseous samples of plasticized PVC film is presented. The detection principle makes use of a direct molecular recognition of the carbonate ion by a molecular tweezer-type ionophore, which has previously been demonstrated to exhibit excellent carbonate selectivity. The carbonate ion is extracted together with hydrogen ions into a polymeric film that contains the anion exchanger tridodecylmethylammonium chloride, a lipophilic, electrically charged, and highly basic pH indicator, which is used for the readout in absorbance mode, in addition to the lipophilic carbonate ionophore. According to known bulk optode principles, such an optical sensor responds to the product of the carbonate ion activity and the square of hydrogen ion activity. This quantity is thermodynamically linked to the activity of carbon dioxide. This allows one to realize a direct carbon dioxide sensor that does not make use of the traditional Severinghaus sensing principle of measuring a pH change upon CO_2 equilibration across a membrane. A selectivity analysis shows that common ions such as chloride are sufficiently suppressed for direct PCO_2 measurements in freshwater samples at pH 8. Chloride interference, however, is too severe for direct seawater measurements at the same pH. This may be overcome by placing a gas-permeable membrane over the optode sensing film. This is conceptually confirmed by establishing that the sensor is equally useful for gas-phase PCO_2 measurements. As expected, humid air samples are required for proper sensor functioning, as dry CO_2 gas will not cause any signal change. The sensor showed acceptable response times and good reproducibility under both conditions.
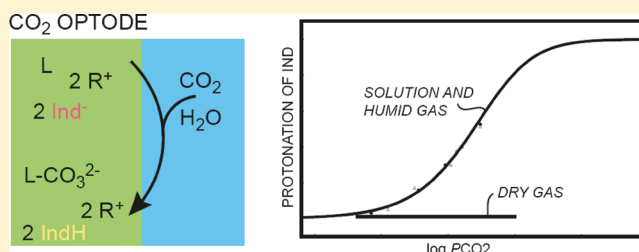
As one of the culprits responsible for the greenhouse effect, carbon dioxide is receiving significant attention from the scientific community and political leadership. Monitoring CO_2 levels in the atmosphere and aquatic environments is therefore an urgent and important task. CO_2 sensors are important tools with increasing relevance to measure the gas concentration in air, in bioprocesses, and as dissolved CO_2 in real process liquids. Generally, however, CO_2 is a poorly reactive molecule, and the direct molecular recognition of CO_2 is difficult to accomplish. Membrane-covered electrochemical CO_2 sensors based on the Severinghaus principle and solid electrolyte sensors operating at high temperatures have been widely applied for a long time.[1] Other measuring methods based on infrared and nondispersive infrared spectroscopy, photoacoustic effects, and thermal conductivity are increasingly being used.[2−5] While Severinghaus-based electrochemical sensors are inexpensive and relatively simple, the CO_2 partial pressure is still determined by monitoring indirectly the pH values of a hydrogen carbonate solution and other similarly behaving dissolved gases may potentially interfere with this measurement principle. Unfortunately, there seems to be a lack of reports on CO_2 sensors based on direct molecular recognition.

Since Severinghaus-type potentiometric probes require a low sample pH (<5.5) for optimal operation, their sensitivity deteriorates at the higher pH value of typical aquatic systems.[6,7]

Under such circumstances, the abundance of carbonate becomes higher and one may consider the analysis of carbonate instead of carbon dioxide gas itself. For this purpose, a highly selective receptor for carbonate is required to reduce interference from other species in natural water samples. Indeed, carbonate selective receptors have been developed that bind with carbonate through hydrogen bonding or reversible covalent bonding.[8−10] A few years ago, a new ionophore with a very high selectivity for carbonate was developed by the group of Nam and was successfully applied in ion-selective electrodes to determine oceanic carbon dioxide.[11] The compound contains two trifluoroacetophenone moieties that interact selectively with CO_3^{2-} to form a 1:1 complex. By utilizing this ionophore, we report here on a CO_2-selective optical sensor that works on the basis of a selective molecular recognition. To our knowledge, this is the first report of such an optical CO_2 sensor system.[12,13]

A traditional PVC-plasticizer bulk optode usually consists of a pH indicator, also referred to as chromoionophore, an ion-exchanger, and an ionophore specific for the analyte.[14,15] As

optical counterparts of ion-selective electrodes, optodes may be developed for the analysis of ionic species. The response mechanism depends on a mass transfer between the sensing film (or particle) and the sample. There are two key modes of mass transfer for ion-selective optodes, one being ion-exchange between sample analyte and protons or another reference ion from the sensing phase, and the other the coextraction of analyte together with a counterion from the sample into the sensing phase. Either way, the degree of protonation of an indicator dye (also called chromoionophore) changes as a function of analyte concentration. These response principles may be optimized by adjusting the sensing phase composition, including the use of ion-exchangers.[14] A wide range of chromoionophores is commercially available, and the associated pK_a values can be determined by the so-called sandwich membrane method.[16]

This paper introduces a carbon dioxide sensing principle based conceptually on the concurrent extraction of CO_2 and H_2O into the sensing phase, yielding carbonate and protons as part of the established dissociation process that are each selectively recognized by an ionophore.

■ THEORY

Carbon dioxide is known to undergo pH-controlled dissociation reactions.[17] The value of K_{a1} relates to the sum of hydrated carbon dioxide and carbonic acid, while the carbonic acid amounts to just 0.2% of this sum, so the relevant equilibria can be expressed as:

$$CO_2(aq) \underset{}{\overset{H_2O}{\rightleftharpoons}} HCO_3^-(aq) + H^+(aq)$$
$$\rightleftharpoons CO_3^{2-}(aq) + 2H^+(aq) \tag{1}$$
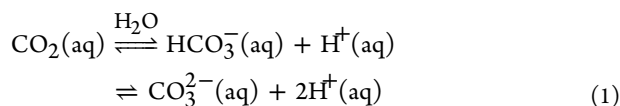
Consequently, the carbon dioxide activity in water is related to the carbonate ion activity as a function of the solution pH and the two stepwise acid dissociation constants as follows:

$$a_{CO_2} = \frac{a_{CO_3^{2-}}(a_{H^+})^2}{K_{a1}K_{a2}} \tag{2}$$

Ionophore-based optical sensors often make use of a H^+-selective chromoionophore (a lipophilic pH indicator, Ind^-) to visualize the ion extraction process. Anionic analytes A^{z-} may be measured according to the following electrolyte coextraction equilibrium, in which the aqueous anion is extracted together with protons into a solvent polymeric phase that contains an anion ionophore, L, that complexes and stabilizes the analyte with a complex stoichiometry 1:n, and the indicator that binds the proton:

$$A^{z-}(aq) + nL(org) + zH^+(aq) + zInd^-(org)$$
$$\rightleftharpoons AL_n^{z-}(org) + zIndH(org) \tag{3}$$
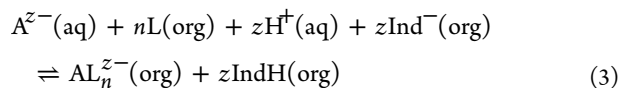
The protonation of the indicator is followed spectroscopically and indicates the level of extraction. If ion pairing in the sensing phase is inconsequential, the corresponding coextraction constant may be formulated:

$$K_{coex} = \frac{1}{a_{A^{z-}}(a_{H^+})^z} \frac{[AL_n^{z-}][IndH]^z}{[L]^n[Ind^-]^z} \tag{4}$$

where species in square brackets denote concentrations in the sensing phase while aqueous species are indicated with activity

symbols. The mass balance condition for the ionophore is written as:

$$L_T = [L] + n[AL_n^{z-}] \tag{5}$$

where L_T is the total ionophore concentration in the membrane. Similarly, the charge balance equation is given as:

$$R_T = [Ind^-] + z[AL_n^{z-}] \tag{6}$$

where R_T is the anion-exchanger concentration. Equations 4−6, together with the relevant mole fractions of indicator ($[IndH] = (1-\alpha)Ind_T$; $[Ind^-] = \alpha Ind_T$) gives the response function of the optical sensor as a function of the mole fraction of unprotonated indicator dye, α:

$$a_{A^{z-}}(a_{H^+})^z = \left(\frac{1-\alpha}{\alpha}\right)^z$$
$$\frac{R_T - \alpha Ind_T}{zK_{coex}\left(L_T - \frac{n}{z}(R_T - \alpha Ind_T)\right)^n} \tag{7}$$

If the analyte is the carbonate anion, eq 7 may equally be expressed as a function of carbon dioxide concentration by incorporating eq 2 to give an optode response function that is now independent of solution pH:

$$a_{CO_2} = \left(\frac{1-\alpha}{\alpha}\right)^2$$
$$\frac{R_T - \alpha Ind_T}{2K_{a1}K_{a2}K_{coex}^I\left(L_T - \frac{1}{2}(R_T - \alpha Ind_T)\right)^2} \tag{8}$$

Of course, the ratio of carbon dioxide activity to carbonate ion activity that gives the same optode response is directly related in eq 2 and depends on the solution pH:

$$\frac{a_{CO_2}}{a_{CO_3^{2-}}} = \frac{(a_{H^+})^2}{K_{a1}K_{a2}} \tag{9}$$

Quite generally, the selectivity of an ion optode can be conveniently expressed as the ratio of the two anion activities (analyte ion activity divided by the interfering ion activity) that, separately measured, give the value of α (which is used as a normalized sensor response). The carbon dioxide response was obtained by considering eq 7 for carbonate and by inserting eq 2 while the interfering ion response was described, simplistically, by assuming that the interfering anion forms 1:1 complexes with the ionophore. This latter assumption is arbitrary and was not tested experimentally, but note that the stoichiometry changes will not significantly change the observed sensor selectivity for a given sensing phase composition. The selectivity of the sensor for carbon dioxide

over another potentially interfering anion is subsequently predicted as follows:[18]

$$k_{CO_2,J}^{OSel} = \frac{a_{CO_2}}{a_J^{n-}}$$

$$= \left(\frac{1-\alpha}{\alpha}\right)^{2-z}(a_{H^+})^z$$

$$\frac{zK_{coex}^J\left(L_T - \frac{1}{z}(R_T - \alpha Ind_T)\right)^z}{2K_{a1}K_{a2}K_{coex}^I\left(L_T - \frac{1}{2}(R_T - \alpha Ind_T)\right)^2} \tag{10}$$

where k^{OSel} is the selectivity coefficient,[18] and the overall extraction constant for carbon dioxide is denoted with a superscript I, while the one for the interfering ion is labeled with J. For divalent interfering anions, eq 10 simplifies to the following relationship:

$$k_{CO_2,J}^{OSel} = \frac{a_{CO_2}}{a_J^{2-}} = \frac{K_{coex}^J(a_{H^+})^2}{K_{a1}K_{a2}K_{coex}^I} \tag{11}$$

while monovalent interfering ions give the following expression for the selectivity coefficient:

$$k_{CO_2,J}^{OSel} = \frac{a_{CO_2}}{a_J^-}$$

$$= \frac{a_{H^+}}{K_{a1}K_{a2}}\frac{1-\alpha}{\alpha}$$

$$\frac{K_{coex}^J(L_T - (R_T - \alpha Ind_T))}{2K_{coex}^I\left(L_T - \frac{1}{2}(R_T - \alpha Ind_T)\right)^2} \tag{12}$$

which can be approximated as follows for sensing phases where the ionophore is in significant excess to the ion-exchanger and indicator:

$$k_{CO_2,J}^{OSel} \approx \frac{a_{H^+}}{K_{a1}K_{a2}}\frac{1-\alpha}{\alpha}\frac{K_{coex}^J}{2K_{coex}^I L_T} \tag{13}$$

Note that the value of the selectivity coefficient for carbon dioxide over all other ions is always dependent on the solution pH. The selectivity increases with increasing pH and deteriorates under acidic conditions. Interference by other competing anions under acidic conditions could be largely eliminated by coupling the above-mentioned sensor equilibrium to a gas permeation step, for example by the use of a gas- and humidity-permeable membrane placed on the sensing phase or by an intermediate gaseous phase between the aqueous sample and polymeric sensing phase.

Alternatively, the sensor approach is expected to work equally well for gas-phase carbon dioxide sensing, in which case the sensor response will be codependent on the humidity of the gas phase. For this case, the overall equilibrium (adapted from eq 3) can be rewritten as:

$$CO_2(g) + H_2O(g) + nL(org) + zInd^-(org)$$

$$\rightleftharpoons CO_3L_n^{2-}(org) + 2IndH(org) \tag{14}$$
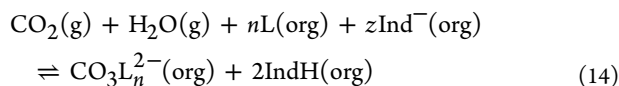
The partition coefficient of carbon dioxide gas between the gas and sensing phase,

$$K_{CO_2} = \frac{a_{CO_2}(org)}{PCO_2} \tag{15}$$

is combined with a similar relationship for the partitioning of humidity,

$$K_{H_2O} = \frac{a_{H_2O}(org)}{PH_2O} \tag{16}$$

to give the sensor response to PCO_2 in the gas phase:

$$PCO_2 = \left(\frac{1-\alpha}{\alpha}\right)^2\frac{R_T - \alpha Ind_T}{2K_{overall}\left(L_T - \frac{1}{2}(R_T - \alpha Ind_T)\right)^2} \tag{17}$$

where $K_{overall}$ is a constant incorporating the partition coefficients for H_2O and CO_2 as well as the acidity constant of the indicator and stability constant of the carbonate ionophore. One may write down a thermodynamic cycle to show that a three-phase system consisting of an aqueous electrolyte in contact with a gas phase and the sensing phase. If all phases are at equilibrium, one should obtain the same optical sensing response, independent of whether this response is related to the carbon dioxide partial pressure in the gas phase or aqueous phase. A reduction of humidity in the gas phase is expected to attenuate the sensor response.

■ EXPERIMENTAL SECTION

Reagents. Aqueous solutions were prepared by dissolving the appropriate salts in Milli-Q purified water. All solvents and reagents used were analytically pure unless otherwise specified. Poly(vinyl chloride) (PVC, high molecular weight), *o*-nitrophenyl octyl ether (*o*-NPOE), bis(2-ethylhexyl) adipate (DOA), chromoionophore IV (ETH 2412), tridodecylmethylammonium chloride (TDDMACl), 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), and tetrahydrofuran (THF) were obtained from Sigma-Aldrich. Carbon dioxide (5.0 vol% in nitrogen) and nitrogen gas (99.9 vol%) were purchased from PenGas in Switzerland. Carbonate selective ionophore VII was purchased from Fluka.

Apparatus. pH values were determined using a Metrohm 826 pH meter. Spectrophotometric studies on optode membranes were performed with a conventional double-beam spectrophotometer (Perkin-Elmer Lambda 2 UV/vis spectrophotometer). The membrane was spin-coated on a glass plate that was mounted into the measuring cell and placed into the spectrophotometer. The flow cell has been previously described[14] (see Scheme S1 in the Supporting Information), but the second glass plate here was left uncoated. CO_2 and N_2 gas were mixed in a gas mixing chamber with a magnetic stirring bar, and the gas mixture was subsequently bubbled into a sample compartment in contact with the sample that was passed into the measuring cell fluidically. The measuring compartment was filled with the same gas mixture, and the tubing that connected the sample compartment and measuring compartment was covered with the same gas mixture to ensure no CO_2 diffusion during the transportation and measurement. The flow rate was controlled by a four-channel IPC microprocessor-controlled dispensing pump from Ismatec. All
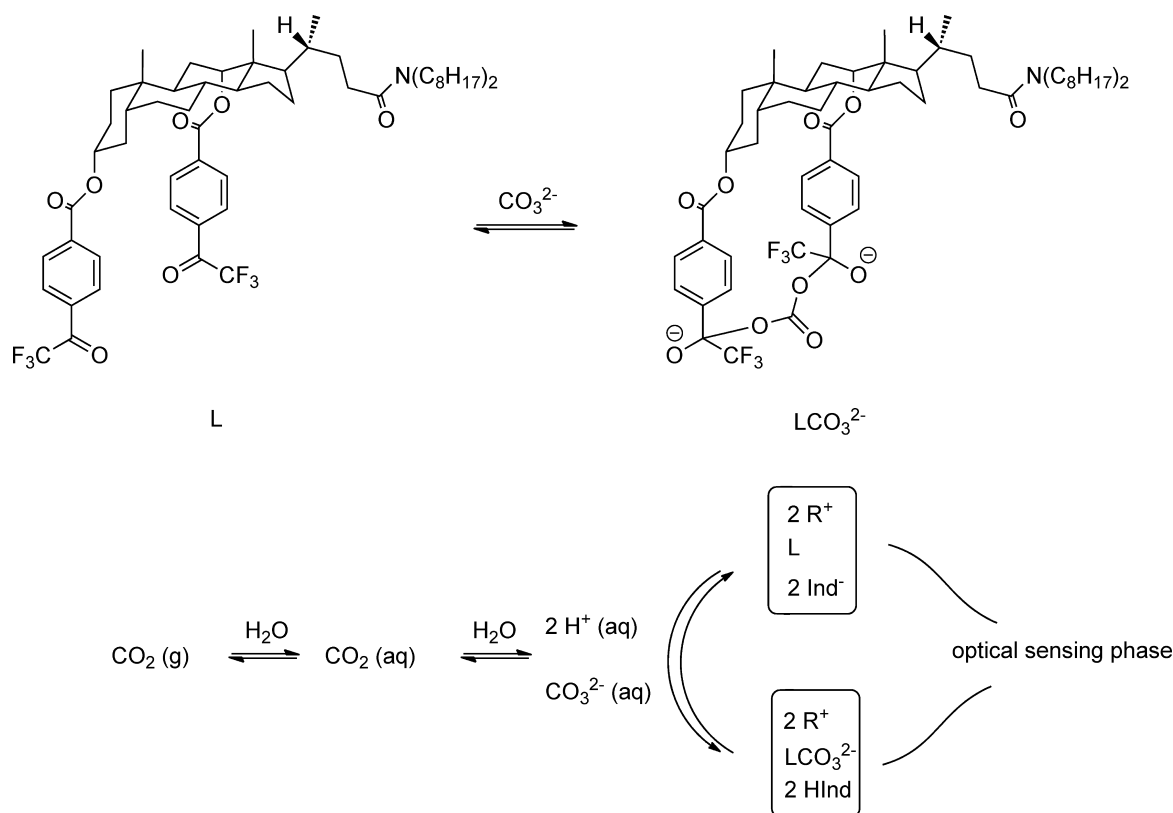
Figure 1. Illustration of sensor mechanism in aqueous and gaseous phase and interaction between the carbonate selective ionophore and CO_3^{2-}. Before exposure to carbon dioxide, the deprotonated, negatively charged indicator Ind$^-$ form the counterion of the anion-exchanger R$^+$ in the sensing film, while the carbonate ionophore L remains uncomplexed and therefore electrically neutral. Upon carbon dioxide extraction, this counterion is replaced by the doubly negatively charged carbonate–ionophore complex, while the indicator becomes the neutral, protonated Hind species.

experiments were performed at 25 ± 1 °C unless otherwise stated.

Membranes and Measurements. For optode membrane preparation, a total amount of 140 mg of high molecular weight PVC and o-NPOE (1:2 by weight), 15 mmol/kg (total mass of sensing film) ETH 2412 (HInd), 15 mmol/kg TDDMACl, and 15 mmol/kg carbonate-selective ionophore were dissolved in 1 mL of THF. A minor mismatch between ion-exchanger and indicator has only a minor influence on optical sensor response, unlike the behavior of their potentiometric counterparts where complete ionophore-mediated selectivity breakdown may occur.[14] The cocktail was then spin-coated on a specially designed glass plate to allow evaporation of THF. The membrane was washed with 0.05 M NaOH solution before any measurement. The carbonate-selective membranes were prepared by dissolving the mixture composed of 8.3 mg of carbonate ionophore VII, 60 mg of PVC, 2 mg of TDDMACl, and 100 μL of DOA in 2 mL of THF. The cocktail solution was then poured into a glass ring (22 mm in diameter) placed on a slide glass and dried overnight at room temperature under a dust-free environment. Small disks were punched from the cast films and mounted in Ostec electrode bodies (Ostec, Sarganz, Switzerland).

All solutions or gases were pumped through the cell at 3 mL/min flow rate. To ensure the carbon dioxide equilibrium between solution and the air above, the pH value of the hydrogen carbonate solution (10^{-3} M) was monitored along the measurement. Different levels of CO_2 and N_2 were first mixed in the gas mixing compartment and then bubbled

through the hydrogen carbonate solution (10^{-3} M) where the pH and carbonate response were measured with a pH probe and carbonate selective electrodes. After both the pH and carbonate response from the ion-selective electrodes became stable, the solution was pumped into the cell through the plastic tubing placed inside another in which gas with the same PCO_2 value was flowing as protecting layer. The absorbance of the membrane at 550 nm was measured. For the measurement in the gaseous phase, instead of using the solution, the air above the solution was pumped into the cell. For selectivity evaluation, H_3BO_3–NaH_2PO_4 buffer solutions (10^{-3} M) with fixed anion concentration (0.01M) were prepared and pumped through the cell for the measurement under the protection of N_2 with pH values increasing by addition of NaOH (1 M). To show that the sensor response to CO_2 was pH dependent, a 0.01 M NaHCO$_3$ solution was saturated with CO_2 (PCO_2 = 0.05) to reach a stable pH value. Afterward, the solution was diluted with water and reverted to the original PCO_2 value to reach a different pH point. At each point the absorbance at 550 nm was recorded and converted to the $1 - \alpha$ value. To characterize the response time and reproducibility of the sensor, the absorbance of the membrane at 550 nm was recorded while the partial pressure of CO_2 was switched between 0.004 and 0.05 atm.

To evaluate the influence of a different humidity to the sensor response, dry CO_2 gas (PCO_2 = 0.05 atm) and CO_2 gas with 100% relative humidity at 25 °C were guided into the gas mixing chamber and the relative humidity was controlled by changing the flow rate of the above-mentioned two incoming

CO_2 streams and measuring the relative humidity with a commercial hygrometer. After the gas was mixed, it was guided into the measuring cell and the sensor response was recorded. The aqueous sample in Scheme S1 was not needed here; instead, a hygrometer was placed inside the sample container to determine the relative humidity of the gas mixture.

The influence of temperature to the optode response was determined by pumping the solution saturated with CO_2 (PCO_2 = 0.05 atm) at different temperatures (37−19 °C) into the measuring cell where the absorption intensity of the membrane at 550 nm was recorded. The temperature of the solution inside the measuring cell was controlled by a water bath and determined in situ with a thermocouple probe (type J).

■ RESULTS AND DISCUSSION

The speciation of carbon dioxide in aqueous solution depends on its partial pressure, temperature, and acid−base reactions within the solution. At varying ionic strength and pH, carbon dioxide coexists with different concentrations of HCO_3^- and CO_3^{2-}. In turn, the solution pH and the activity of CO_3^{2-} dictate the partial pressure of CO_2. A direct, selective detection of carbon dioxide is possible by extracting the carbonate species together with protons into a sensing film that contains selective receptors for both. Figure 1 illustrates the sensing mechanism for the solution and gas phase. A carbonate-selective ionophore containing two trifluoroacetyl groups anchored onto a steroid backbone to form a molecular tweezer geometry was previously introduced by Nam and co-workers for use in ion-selective electrodes.[19] Indeed, the selectivity of membranes containing this receptor was demonstrated to be very attractive, with carbonate measurements demonstrated in undiluted seawater samples.[11] This tweezer-type ionophore has now become commercially available and explored in an optical carbonate sensor.

As explained in the theoretical section above, a classical bulk optode operating on the basis of the coextraction of an anion with protons should give rise to an optical sensor for the direct detection of PCO_2, independent of solution pH. This sensing principle is attractive because optical detection can be achieved via concentration changes of the lipophilic pH indicator. Protonation of the indicator is ideally only possible by concurrent extraction of carbonate anions and protons.

Initial experiments explored the combination of the carbonate ionophore with the established lipophilic nile blue derivative, ETH 5294, which exhibits a pK_a value of about 14.8 in a PVC−o-NPOE sensing phase.[16] However, extraction of carbon dioxide did only visibly occur above a concentration of 0.07 atm, which is not sufficiently sensitive for practical use. Consequently, a lipophilic pH indicator of a much higher basicity was required to shift the measuring range to environmentally relevant concentrations. An electrically charged base (referring to the nonprotonated form) is expected to increase its pK_a quite dramatically in a nonpolar organic solvent compared to water, because the dissociation equilibrium results in a separation of charge. Indeed, such electrically charged H^{+}-chromoionophores are commercially available, and their pK_a values were quantified in the polymeric sensing phase with the so-called sandwich membrane technique. The chromoionophore ETH 2412, which exhibits a pK_a of 17.0 in PVC−DOS and 20.5 in PVC−NPOE,[16] was chosen for further studies. The use of an electrically charged chromoionophore, along with a neutral carbonate ionophore, necessitates the

addition of a lipophilic anion-exchanger into the sensing film to provide for the cationic counterions of the unprotonated dye.[20] As carbon dioxide is extracted along with protons, the anion-exchanger forms the counterions of the anionic ionophore—carbonate complex instead of the chromoionophore which now becomes neutral. The higher pK_a in PVC−NPOE appeared to be more attractive in view of attaining an adequate operational measuring range and was selected over PVC−DOS.

After the sensing film was solvent cast on a glass plate and fitted into the flow cell system, it was washed with dilute NaOH solution to ensure a complete deprotonation of the chromoionophore in the film. This was especially important for the gas-phase measurements, where contact with aqueous electrolyte was no longer possible during measurement. To perform carbon dioxide measurements appropriately, the initial 5 vol% CO_2 gas was diluted with nitrogen and equilibrated with the aqueous solution in a closed cell, which was subsequently guided to the measurement cell. The corresponding optode response curves to aqueous carbon dioxide were obtained by determining the α value from the absorbance changes of the film and are shown in Figure 2. The use of the more basic
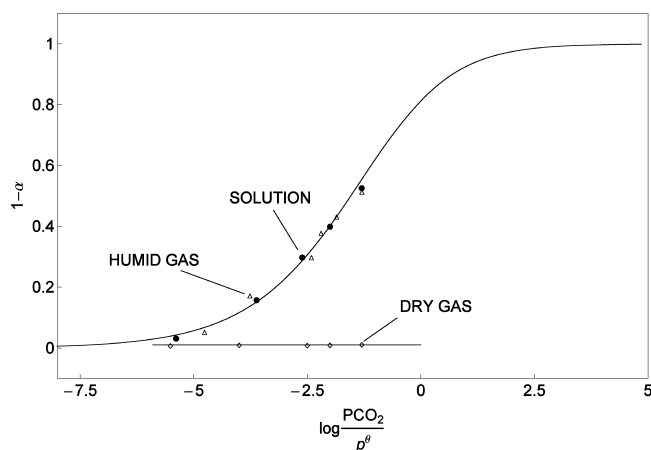

Figure 2. Calibration curves of the sensor response to CO_2 in a 10^{-3} M hydrogen carbonate solution, the gas phase above 10^{-3} M hydrogen carbonate solution, and dry $CO_2 + N_2$ gas mixture with different levels of PCO_2. The absorbance of the sensing film at 550 nm was converted into the mole fraction of protonated indicator, $1 - \alpha$, and shown as symbols with theoretical expectations according to eq 7 (lines). The term p^θ on the x-axis is the partial pressure under standard conditions (1 atm).

chromoionophore indeed shifts the measuring range to lower PCO_2 values. Atmospheric PCO_2 is currently at about 380 ppm or 0.04% by volume. The lowest concentration measured and presented in Figure 2 is 3×10^{-4} % by volume, while the detection limit (3 × SD of the background) is estimated as 200 ppm. This appears to be adequate for routine environmental monitoring, although a further optimization of the measuring range would certainly be possible if needed by adjustment of the sensing film composition.

Equation 8 postulates that if the optical sensor responds to the product of the carbonate ion concentration and the square of the hydrogen ion activity, this should be independent of pH, i.e., the α value (mole fraction of unprotonated indicator, calculation shown in the Supporting Information) should be the same at different pH value as long as PCO_2 stays constant. To confirm this assumption experimentally, the absorbance of the sensing film at 550 nm was recorded at the same partial

pressure of carbon dioxide (0.05 atm) while the sodium hydrogen carbonate solution was diluted with water to reach lower pH values. At each dilution step, the solution was equilibrated with carbon dioxide from the gas phase before measurement. If the sensor response would be pH dependent, one would expect a dramatic decrease of α value. However, as shown in Figure 3, the α value was indeed found to be independent of pH, supporting the optode response mechanism proposed here.
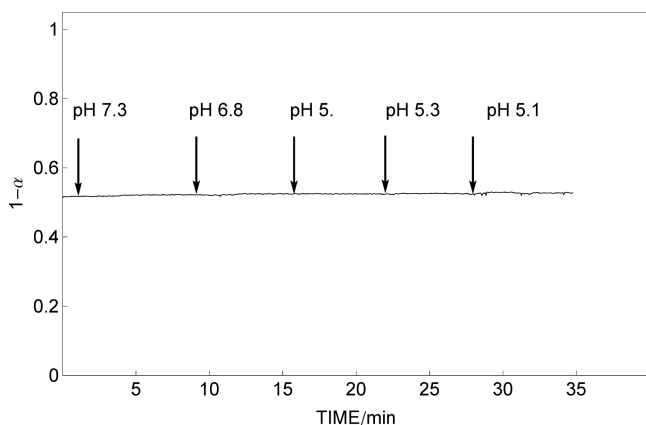

Figure 3. Evidence showing the pH independence of the carbon dioxide sensor in accordance to eq 8. PCO_2 was fixed at 0.05 atm above the hydrogen carbonate solution (10^{-3} M). The solution was diluted by addition of water to reach different pH values while maintaining an equilibration with the contacting gas phase.

The tweezer-type ionophore was demonstrated to exhibit excellent selectivity when used in ion-selective electrode membranes, but the ionophore had, so far, never been explored in an optical sensor or for the direct detection of carbon dioxide. The selectivity was characterized by evaluating the response to solutions of separate electrolytes. Specifically, and in agreement with earlier procedures, the measurements were performed in contact with buffer solutions at varying pH but at a fixed 0.01 M anion concentration. Figure 4 shows the data together with the theoretical curves according to eq 7 to obtain the coextraction constants for each anion–proton pair. The curves correlate well with experimental data except for sulfate,
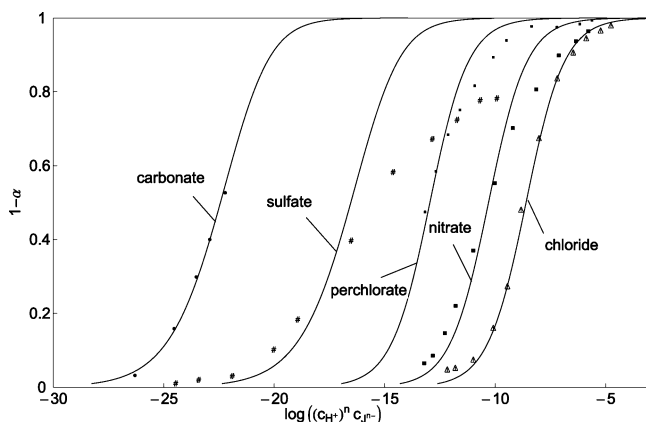

Figure 4. Response of the optode membrane to pH (symbols) in 10^{-3} M H_3BO_3–NaH_2PO_4 buffer solutions containing the indicated anions fixed at 0.01 M. The pH of the solution was increased by adding 1 M NaOH.

possibly because of partial protonation of this anion in the sensing phase, which the theory is not considering.

For a better representation of selectivity, a plot of the sensor response against the logarithm of analyte activity at pH 8 is shown in Figure 5. As pointed out in eq 10, even though the
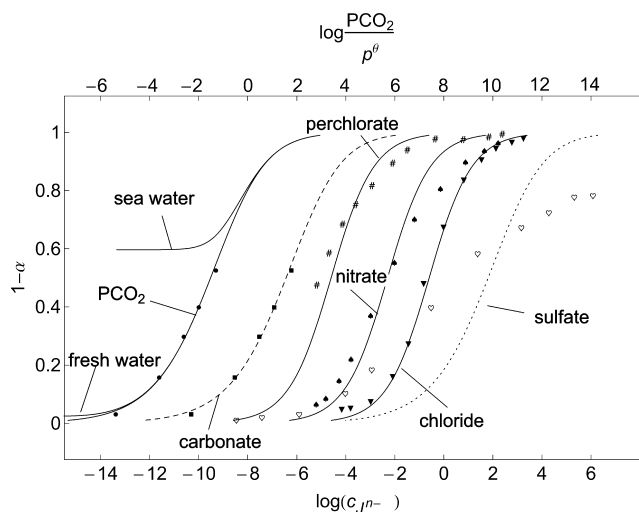

Figure 5. Presentation of sensor selectivity for carbon dioxide at pH 8 using the theoretical curves from Figure 2. The PCO_2 responses for seawater and freshwater solutions relate to the upper x-axis while the anion concentrations are described by the values on the lower x-axis. The carbonate ion is added to compare the selectivity between this anion and other potentially interfering anion species. It should not be used to infer a sensor selectivity of carbon dioxide over carbonate, because this shift is only due to the relevant protonation equilibria (see text).

CO_2 response is pH independent, the selectivity depends on the sample pH. At pH 8, the selectivity coefficient for carbonate over chloride is around 6 orders of magnitude, which agrees with the previous report for this tweezer-type ionophore in ion-selective membranes. Because eq 10 is used to express carbon dioxide, the selectivity for carbonate and CO_2 will run in the opposite direction. For increasing pH, the selectivity for CO_2 improves while for carbonate, it deteriorates, and vice versa for lower pH values (see Supporting Information). The chloride concentration in surface fresh water is typically in a range of 0.1 to 0.6 mmol/L,[21,22] and Figure 5 shows that these conditions give minimal interference ($1 - \alpha \approx 0.02$ to 0.05). This means that chloride interference in fresh water will be sufficiently suppressed for direct CO_2 measurement at the typical environmental pH of 8. However, seawater contains much more chloride than fresh water (average: 545 mmol/L)[21] and will cause severe interference at the same pH. At higher pH, the selectivity improves (see Supporting Information). This may necessitate the placement of a gas-permeable membrane on the sensing film, essentially blocking the extraction of ionic species into the sensing film. While this is a common strategy for many potentiometric carbon dioxide sensors, the selectivity of the system described here is expected to be more attractive based on a direct molecular recognition of the analyte species.[23]

As shown in Figure 2, the sensor responds to humid carbon dioxide gas in a manner similar to that for dissolved carbon dioxide. The observed difference points to a diminished water activity in the gas phase. Indeed, removing the humidity by using dry gas completely suppresses the dissociation equilibria that are required to form the carbonate and proton species that

are required for the sensor response. This is conceptual evidence that a gas-permeable membrane placed between the sample and the sensing phase will allow one to reliably measure carbon dioxide even in the high chloride concentration of seawater.

The response time of the membrane is affected by diffusion process and also the thickness of the membrane. Response time is expected to decrease with a kinetically rapid coextraction (and hence molecular binding/dissociation process) and a decreasing thickness of the sensing film. Even though the sensing films studied here did not exhibit optimal thickness (3.0 μm via absorbance measurements and applying Beer's law), a reasonable response time was observed, see Figure 6, that
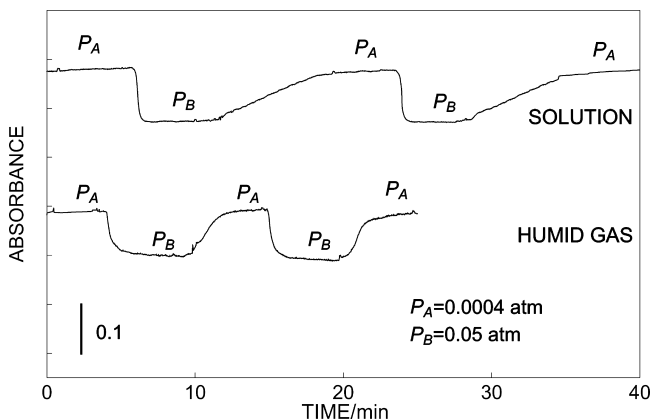

Figure 6. Top: response time of the sensor in contact with an aqueous 10^{-3} M hydrogen carbonate solution equilibrated with PCO_2 of 0.004 and 0.05 atm. Bottom: corresponding experiment in direct contact with a humid gas phase containing the same levels of PCO_2.

suggests mass transport is limited by diffusion in the sensing phase. For this experiment, the carbon dioxide partial pressure was alternated between 0.004 and 0.05 atm, and the aqueous phase was allowed to equilibrate with the aqueous sample before it was fluidically guided into the flow cell to record the sensor response. Note that the measurement in gaseous phase shows a shorter response time than that in solution, suggesting that the optical sensor response is largely diffusion limited.

CONCLUSIONS

A novel direct carbon dioxide sensing method has been presented. Unlike conventional methods based on Severinghaus's principle, molecular recognition between carbonate and a tweezer-type ionophore is used in plasticized PVC films. The optode membrane shows a detection limit of 200 ppm, which should be adequate for routine environmental monitoring. A selectivity analysis shows a satisfactory result for practical CO_2 monitoring in fresh water. Oceanic water usually contains several hundred mmol/L of chloride ions; thus, the chloride interference is detrimental. However, this may be overcome by a direct sensing of a gaseous phase in equilibrium with the sample solution. Indeed, it is conceptually demonstrated that the optode sensing film responded not only to aqueous CO_2 but also to humid CO_2 gas.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: bakker.eric2@gmail.com.

Notes
The authors declare no competing financial interest.

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