

Determination of Oceanic Carbon Dioxide Using a Carbonate-Selective Electrode

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Potentiometric properties of the PVC membrane-based electrodes prepared with molecular tweezer-type neutral carriers, 3,12-bis(TFAB)CA and deoxy-3,12-bis(TFAB)CA, and trifluoroacetyl-*p*-decylbenzene (TFADB) were measured in buffered electrolytes (0.1 M Tris–H₂SO₄, pH 8.6 and 8.0) and artificial seawater. It was observed that the deoxy-3,12-bis(TFAB)CA-based electrode provides greatly enhanced carbonate selectivity over chloride ($\log K_{\text{CO}_3^{2-},\text{Cl}^-}^{\text{POT}} \sim -6$) and other minor anions present in seawater. Thus, we explored the possibility of applying this new carbonate-selective electrode for direct determination of oceanic carbon dioxide. The total carbon dioxide (TCO₂) level in surface Yellow Sea water was determined with the deoxy-3,12-bis(TFAB)CA-based electrode, Severinghaus-type CO₂ gas sensor, and the traditional potentiometric titration methods. The results showed that the carbonate-selective electrode provides accurate oceanic TCO₂ determination comparable to that obtainable with the other two methods. The analytical procedure based on a carbonate-selective electrode is clearly advantageous over other conventional methods: it does not require any sample pretreatment and extra reagents other than the standard calibration solutions, while providing the measured results directly and immediately.

The detailed information about the spatial and temporal variations in inorganic carbons in oceans is very important to map out the global carbon cycle, especially in relation to the air–sea redistribution of the rapidly increasing anthropogenic carbon dioxide in the atmosphere and its influence on the greenhouse effect.^{1–5} The oceanic carbon cycle is usually studied by measuring four parameters: total inorganic carbon, total alkalinity, solution acidity, and carbon dioxide fugacity.^{6–9} With given thermodynamic

constants for carbonic acid in seawater, the oceanic carbon system can be quantified by measuring any two parameters among the four. The choice of parameters largely depends on the attainable accuracy and precision of available analytical techniques and the simplicity of the measurement methods. For example, the acidity (pH) of seawater is one of the most frequently measured parameters, not only because the value directly reflects the equilibrium state of the oceanic CO₂ system, but also because it is conveniently measured using pH-responsive glass electrodes. Another frequently measured parameter is the total CO₂ (TCO₂) in seawater; it is estimated from the total alkalinity determined by potentiometric titration or from the concentration of dissolved CO₂ measured directly with coulometric methods, infrared spectroscopy, and gas chromatography.^{10–13} However, the measurement of dissolved CO₂ in seawater is not as easy as pH measurement and often requires rather elaborate instrumentation. Optical and various electrochemical (e.g., potentiometric, coulometric, and amperometric) carbon dioxide sensors, which are based on the Severinghaus-type structure, are also often used to directly measure the dissolved CO₂ gas in seawater.^{14–17} These sensors, however, provide limited analytical performance in real seawater analysis, because they exhibit a reduced sensitivity to dissolved CO₂ at the normal pH range of seawater (ca. 8.0), a slow response time, and an unstable signal.

Under normal seawater conditions (pH 8.0–8.2), CO_{2(aq)} is a minor species (<1%), and the concentration of CO₃^{2–} is ~10 to 11% of the total inorganic carbons. Hence, considering the relative abundance of CO₃^{2–} ion in seawater, carbonate-selective electrodes should find their use in seawater analysis. However, the carbonate selectivity of the electrodes based on trifluoroacetophenone (TFAP) derivatives (e.g., trifluoroacetyl-*p*-butylbenzene or -*p*-decylbenzene; TFABB or TFADB), the best-known carbonate-selective neutral carriers, seems not sufficiently high to use with solutions with a high ionic strength, such as seawater.¹⁸

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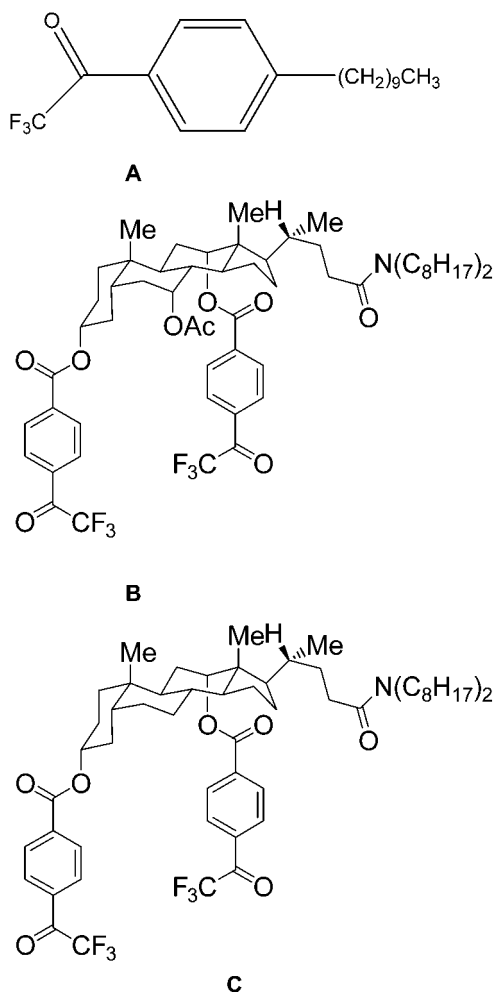


Figure 1. Structures of the three carbonate-selective neutral carriers examined in this study: A, trifluoroacetylphenyl-*p*-decylbenzene; B, *N,N*-diethyl-7 α -acetoxy-3 α ,12 α -bis(4-trifluoroacetylbenzyloxy)-5 β -cholan-24-amide [denoted as 3,12-bis(TFAB)CA in the text]; and C, *N,N*-diethyl-3 α ,12 α -bis(4-trifluoroacetylbenzyloxy)-5 β -cholan-24-amide [denoted as deoxy-3,12-bis(TFAB)CA].

Recently, we synthesized a series of new carbonate-selective neutral carriers that behave like molecular tweezers; two or three TFAP groups are attached to a rigid frame molecule, e.g., cholic acid.¹⁹ It was observed that the carbonate selectivity of the electrode based on *N,N*-diethyl-7 α -acetoxy-3 α ,12 α -bis(4-trifluoroacetylbenzyloxy)-5 β -cholan-24-amide [3,12-bis(TFAB)CA] over chloride ($K_{\text{CO}_3^{2-},\text{Cl}^-}^{\text{POT}} = 2 \times 10^{-6}$) and other common anions appears to be high enough to apply to seawater analysis. Further investigations on cholic acid-based TFAP derivatives found another neutral carrier, *N,N*-diethyl-3 α ,12 α -bis(4-trifluoroacetylbenzyloxy)-5 β -cholan-24-amide [deoxy-3,12-bis(TFAB)CA] (Figure 1),²⁰ that provides improved potentiometric performance over 3,12-bis(TFAB)CA in terms of its carbonate selectivity over lipophilic anions (e.g., salicylate, ClO_4^- , and SCN^-). We, thus, prepared the carbonate-

selective electrodes with TFADB, 3,12-bis(TFAB)CA, and deoxy-3,12-bis(TFAB)CA and attempted to measure the carbonate concentrations in seawater with those electrodes. The results clearly demonstrate that the carbonate-selective electrodes based on molecular tweezer-type neutral carrier provide fast, convenient, and accurate results for the determination of TCO_2 in seawater.

EXPERIMENTAL SECTION

Reagents. Poly(vinyl chloride) (PVC), tridodecylmethylammonium chloride (TDMACl), and bis(2-ethylhexyl) adipate (DOA) were purchased from Fluka Chemie AG (Buch, Switzerland). Trifluoroacetyl-*p*-decylbenzene (TFADB) was from Trans World Chemicals (Rockville, MD). *N,N*-Diethyl-7 α -acetoxy-3 α ,12 α -bis(4-trifluoroacetylbenzyloxy)-5 β -cholan-24-amide [3,12-bis(TFAB)CA], *N,N*-diethyl-3 α ,12 α -bis(4-trifluoroacetylbenzyloxy)-5 β -cholan-24-amide [deoxy-3,12-bis(TFAB)CA] were synthesized and purified as described in the literature.^{20,21} 2-Amino-2-hydroxymethyl-1,3-propanediol (TRIS) and 2-aminopyridine (AMP) were obtained from Sigma Chemical Co. (St. Louis, MO).

All other chemicals were analytical grade and were used without further purification. All solutions were prepared with deionized water (18 $\text{M}\Omega\cdot\text{cm}$) and were stored in tightly closed vessels for later use.

Artificial Seawater and Buffer Solutions for Electrode Calibration. The recipe for artificial seawater (ASW) of salinity $S = 35$ ‰ was taken from reference 22. For pH electrode calibration, standard pH buffer solutions were prepared with the recipe of ASW given in the reference by Dickson and Goyet (D & G), replacing an appropriate amount of NaCl (0.04 molal) with HCl and by adding desired base (0.08 molal Tris or AMP) to the solution.²³ The salinities of Tris/HCl and AMP/HCl buffer solutions were adjusted to a desired value (e.g., $S = 33.0$ ‰, the approximate salinity of the Yellow Sea in Korea) by changing the amount of NaCl from the exemplary composition given in references 22 and 23. The pH values of standard Tris and AMP buffers, 8.05 and 6.76, respectively, at $S = 33.0$ ‰ and at the temperature 26 ± 0.1 °C were also determined using the methods given in D & G.²³

Preparation of the Electrodes and Their Potentiometric Evaluation. The carbonate-selective membranes were prepared from the mixture composed of 8.3 mg of TFAP derivatives (TFADB, 3,12-bis(TFAB)CA and deoxy-3,12-bis(TFAB)CA), 60 mg of PVC, 2 mg of TDMACl, 100 μL of DOA, and 300 μL of ethyl acetate.¹⁹ The cocktail solutions dissolved in 0.5 mL of THF were then poured into a glass ring (22 mm) 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 Philips electrode bodies (IS-561; Glasblaserei Möller, Zürich, Switzerland). For all electrodes, a mixture containing NaH_2PO_4 (0.1 M), Na_2HPO_4 (0.1 M), and NaCl (0.01 M) was used as the internal filling electrolyte. Potentiometric evaluations for the electrodes were carried out as described previously using a static

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arrangement;¹⁸ potential differences between the electrodes and the Orion sleeve-type double-junction Ag/AgCl reference electrode (model 90-02) were measured using a PC equipped with a high-impedance input 16-channel analog-to-digital converter (Multi pH/Ion meter KST101B, Kosentech, Busan, Korea).

Response and calibration curves were obtained by adding standard solutions (calculated aliquots of 0.01, 0.1, and 1 M NaHCO₃) stepwise to 200 mL of magnetically stirred background electrolyte (e.g., 0.1 M Tris-H₂SO₄, pH 8.6; 0.1 M Tris-H₂SO₄, pH 8.0; artificial seawater with salinity 33.0 ‰ and 35.0 ‰; 0.2 M citric acid, pH 5.0). The measurements were carried out in closed beakers with a specially designed top to avoid interference from atmospheric carbon dioxide. Activities of carbonate and other anions [e.g., Cl⁻, Br⁻, NO₃⁻, NO₂⁻, SCN⁻, salicylate (Sal⁻), ClO₄⁻] in 0.1 M Tris-H₂SO₄ were calculated as described in reference 24. The pH responses of the ion-selective electrodes (ISEs) were obtained by titrating a buffer composed of 1.4 mM boric acid, 6.7 mM citric acid, and 10 mM sodium dihydrophosphate (pH 2.8) with small aliquots of 0.1 M NaOH while simultaneously monitoring the pH of the solution with an Orion combination glass pH electrode (model 9155).

Potentiometric measurements on seawater samples from the Yellow Sea (the west coast of Korea) were made with carbonate-selective electrodes; the seawater sample (~100 mL) was taken out of the tightly sealed polyethylene bottle and poured into a beaker (100 mL) equipped with a top, and the potentiometric measurement was made as quickly as possible to minimize the change in CO₂ content in the sample. For comparison, the seawater sample was mixed with an equal volume of 0.2 M citric acid (pH 5.0) in a closed cell, and the concentration of carbon dioxide was measured with the Severinghaus-type electrode (model 95-02, Orion Research Inc., MA).

Determination of Chlorinity and Salinity of Yellow Sea Water Samples. Samples of surface Yellow Sea water were collected at the coast of Jebudo, an island located ~100 km from our laboratory (Seoul), following the recommended procedure.²³ Seawater samples were collected in 15 polyethylene bottles (2 L volume) leaving about 1% of headspace, sealed with paraffin film and a gastight cap, kept in the ice box during 2 h of transportation, and warmed to room temperature in a thermostat before the measurement in the laboratory. All samples were used up within 12 h to minimize the contamination from microorganisms in the sample.

The determination of chlorinity in seawater samples was performed by means of a silver nitrate titration using a modified Mohr-Knudsen method.²⁵ In our experimental setup, the mean volume of titration (V_{mean}) for standard ASW was 11.7 mL, which yields a buret correction factor (f) of 1.66; for the Yellow Sea water V_{mean} was 10.9 mL, which yielded a chlorinity (Cl) of 18.0. The salinity of Yellow Sea was calculated with the relationship $S = 1.80655 \times Cl$ (‰) as given in reference 25, yielding a salinity of 32.6 ‰. These values were used to estimate the total carbon dioxide from the total alkalinity determined with the potentiometric titration.

Determination of Total Dissolved Inorganic Carbon (TCO₂) with Potentiometric Titration in a Closed Cell. The potentiometric titration of seawater samples was performed in a closed cell equipped with magnetic stirrer at constant temperature ($t = 26 \pm 0.1$ °C). A 100.0 mL sample of seawater was transferred to the titration cell while making all efforts to avoid the dissolution of atmospheric carbon dioxide. The combination pH electrode was calibrated before titration using TRIS and AMP buffer solutions with salinity $S = 33.0$ ‰. A solution of hydrochloric acid (0.02 mol/kg-soln), whose total ionic strength was adjusted to approximately that of seawater ($I = 0.67$ mol/kg-soln) with 0.70 mol/kg-soln NaCl, was used as the titrant; the stable pH and potential values were recorded at every 300 μ L interval, and the titration was continued until the pH of the solution dropped below 3.

After the titration, the data were processed using the program listed in the reference by D & G;²³ however, the program was modified for MATLAB (version 6.0, The Mathworks, Inc.) and used the NLINFIT standard routine from the statistics toolbox for nonlinear fitting of the data. The detailed procedures for the total alkalinity and TCO₂ calculations are lucidly explained in the reference by D & G. All necessary information regarding oceanic CO₂ calculations can also be gotten from the website.²⁶

RESULTS AND DISCUSSION

Potentiometric Evaluation for the Bis(TFAB)CA-Based Carbonate-Selective Electrodes. Figure 1 shows the structures of three carbonate-selective neutral carriers used in this study. Because TFADB is the best-known carbonate-selective compound, it was selected as the reference material. It was proposed that two TFADB molecules bind one carbonate ion between the electron-deficient carbonyl carbons.²⁷ 3,12-Bis(TFAB)CA was introduced in our previous report as the molecular tweezer-type carrier: two TFAB groups are framed on a rigid scaffold molecule and may behave like a pair of tweezers for carbonate with an intervening water molecule.¹⁹ Deoxy-3,12-bis(TFAB)CA is very close to 3,12-bis(TFAB)CA in its structure, except that it has no acetate group on the C7 position of the cholic acid backbone; this compound was designed to improve the carbonate recognition ability by removing the bulky acetate group that has no apparent function in the molecule.²⁰

The analytical utility of these carbonate-selective neutral carriers was then examined using the PVC membrane-based ISEs. The membrane compositions were optimized as described in our previous reports,^{18,19} and their potentiometric performance, including carbonate selectivity, was measured first in a 0.1 M Tris-H₂SO₄ buffer (pH 8.6) using the matched potential method suggested by Gadzekpo and Christian. The $K_{\text{CO}_3^{2-},j}^{\text{POT}}$ values were the activity ratio of the carbonate ion and the interfering anion j , which gives the same potential change in a reference solution.²⁸ Figure 2 explicitly shows that the membranes based on molecular tweezer-type compounds provide 10–400-fold improved carbonate selectivity over various anions, as compared to that of the electrodes based on TFADB. Although both bis(TFAB)CA compounds exhibit similar potentiometric performance, as we supposed, the electrode

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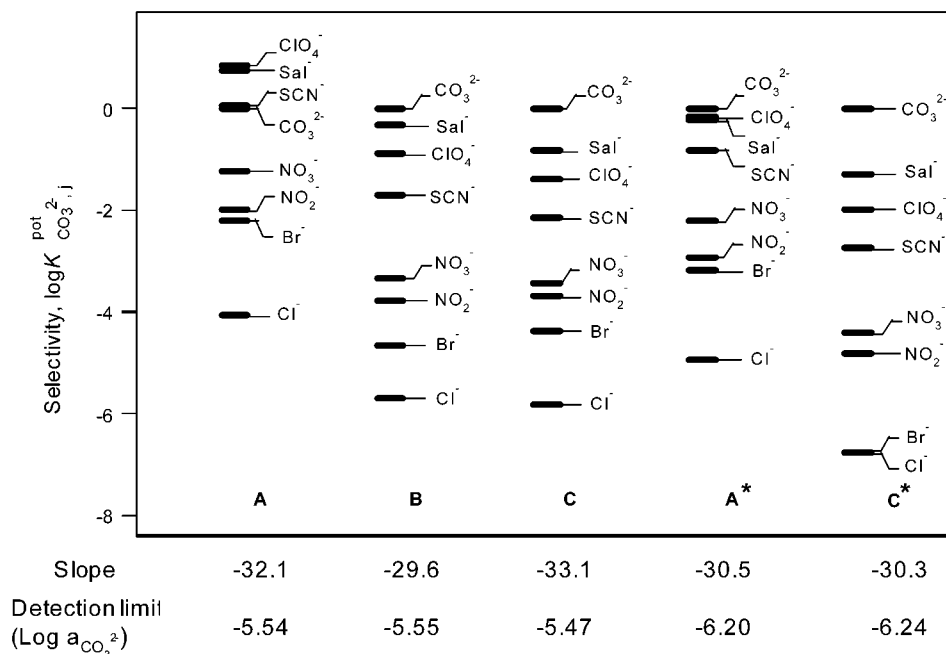


Figure 2. Carbonate selectivity coefficients, response slopes, and detection limits of three trifluoroacetophenone derivative-based electrodes measured at pH 8.6 (0.1 M Tris–H₂SO₄). Electrodes A, B, and C are prepared using the corresponding neutral carriers shown in Figure 1. Asterisk indicates the result obtained at pH 8.0 (0.1 M Tris–H₂SO₄).

based on deoxy-3,12-bis(TFAB)CA provides improved carbonate selectivity over lipophilic anions (e.g., Sal[−], ClO₄[−], and SCN[−]) and Cl[−], as compared to that of the 3,12-bis(TFAB)CA-based one. Hence, further evaluation of the electrode for oceanic carbon dioxide analysis was performed using the electrode based on deoxy-3,12-bis(TFAB)CA.

Since the pH of normal seawater is ~8.0, the carbonate selectivity of the electrode based on deoxy-3,12-bis(TFAB)CA was examined further at pH 8.0 (0.1 M Tris–H₂SO₄ buffer); the results are also included in Figure 2. The carbonate selectivity of the electrode appears substantially improved at pH 8.0; however, there is no evidence that the carbonate binding ability of bis(TFAB)CA compounds is truly enhanced at pH 8.0. Rather, the improved selectivity reflects the changes in the fraction of carbonate (hence, its activity) at a lower pH. The activity of carbonate at pH 8.0 is about one-tenth of that at pH 8.6, but the activities of interfering ions vary little with respect to pH change. Hence, the activity ratios between the carbonate and interfering ions, i.e., the $K_{\text{CO}_3^{2-}, i}^{\text{POT}}$ values, at pH 8.0 are substantially lowered, as compared to those evaluated at pH 8.6, resulting in the apparent enhancement in carbonate selectivity at the lower pH. Figure 3 is the calibration plots of the deoxy-3,12-bis(TFAB)CA-based electrode at pH 8.0. The electrode provides an excellent detection limit (5.8×10^{-7} M) for the carbonate ion and hardly responds to an oceanic level (~0.7 M) of chloride. Considering that the amount of prevalent interfering ions in seawater is drastically low (e.g., the average concentration of NO₃[−] ~ 1–500 μg, NO₂[−] ~ 1–50 μg, and only trace amounts of ClO₄[−], Sal[−], SCN[−] exist), but the average oceanic TCO₂ level is in the 1.8–3 mM range, it is expected that the determination of TCO₂ with the deoxy-3,12-bis(TFAB)CA-based electrode can be easily performed.

Determination of the TCO₂ Level in Seawater. The potentiometric response of the deoxy-3,12-bis(TFAB)CA-based electrode to varying concentrations of TCO₂ was evaluated by adding 1–5

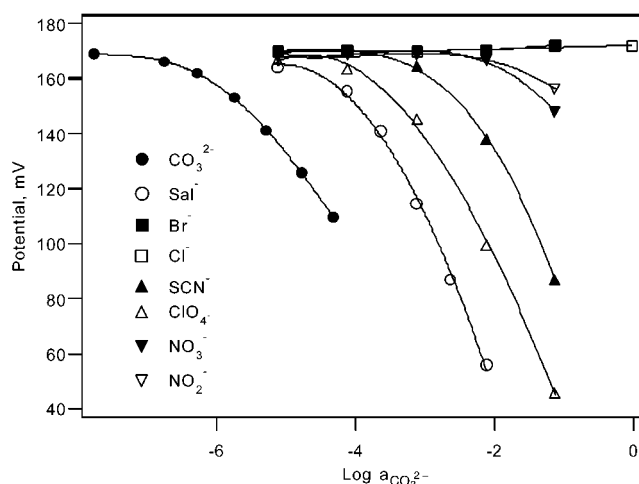


Figure 3. Calibration plots of the deoxy-3,12-bis(TFAB)CA-based electrode to various anions. Background electrolyte, 0.1 M Tris–H₂SO₄, pH 8.0.

mM NaHCO₃ to an artificial seawater (ASW) sample with 35 ‰ salinity. Since the addition of NaHCO₃ also varies the pH, the pHs of the ASW sample were simultaneously monitored using the glass electrode. It is critically important to calibrate the glass electrode with the correct buffer solutions prior to the measurement. As shown in Figure 4, the deoxy-3,12-bis(TFAB)CA-based electrode exhibited stable step responses to varying NaHCO₃ concentrations. Since the deoxy-3,12-bis(TFAB)CA-based electrode exhibited negligible pH response in the pH 6.5–8.5 range, the step responses to varying NaHCO₃ concentration over 1 mM resulted from the change in carbonate concentration. Shown in Figure 4B is the calibration plot of the deoxy-3,12-bis(TFAB)CA-based electrode to varying carbonate activities that are calculated from the dissociation constants of carbonic acid, K_1 and K_2 , defined in the seawater medium.⁸ The response slope of the deoxy-3,12-bis-

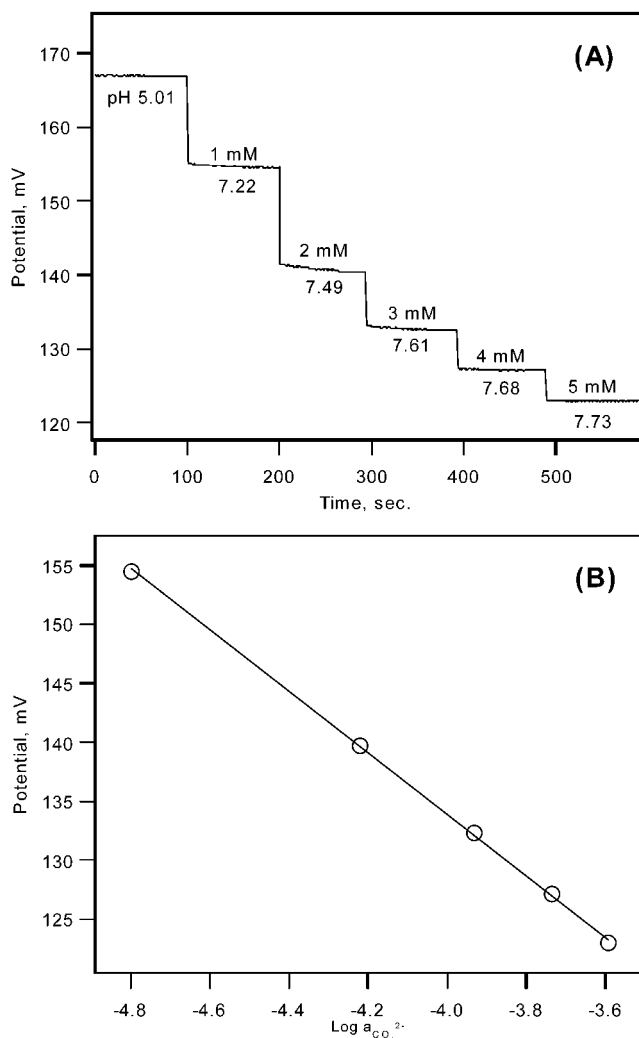


Figure 4. Dynamic response curve (A) and calibration plot (B) of the deoxy-3,12-bis(TFAB)CA-based electrode to varying NaHCO_3 concentrations in artificial seawater (salinity = 35.0 ‰).

(TFAB)CA-based electrode, -26.0 mV/decade, was slightly reduced because of the increased interferences in the seawater medium.

Surface Yellow Sea water samples were collected from the coast located about 100 km from our laboratory, and their TCO_2 levels were determined using the deoxy-3,12-bis(TFAB)CA-based electrode. To determine the level of TCO_2 in the real seawater samples, the carbonate-selective electrode was calibrated first in the ASW having a salinity (33 ‰) similar to that of the Yellow

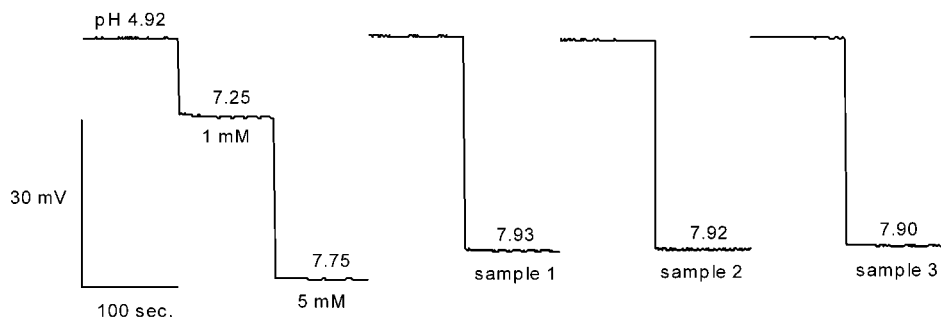


Figure 5. The step response of the deoxy-3,12-bis(TFAB)CA-based electrode to standard calibration solutions prepared with artificial seawater of 33 ‰ salinity and three Yellow Sea water samples.

Table 1. Determination of TCO_2 in Yellow Sea Water with the Deoxy-3,12-bis(TFAB)CA-based Electrode, Severinghaus-type CO_2 Gas Sensor, and a Standard Potentiometric Titration Method²³

method	TCO_2 value determined (mmol/kg seawater)
ISE	1.94 ± 0.03 ($n = 15$)
gas sensor	1.93 ± 0.01 ($n = 3$)
potentiometric titration	1.95 ± 0.04 ($n = 8$)

Sea water (32.6 ‰). The salinity of seawater was predetermined as described in the Experimental Section, and the standard ASW sample was prepared as directed in the reference by D & G. The potentiometric responses were then measured by alternately changing the sample solutions from standard ASW to real seawater. Figure 5 displays the response curves obtained with the deoxy-3,12-bis(TFAB)CA-based electrode; it is seen that the electrode provides fast, stable, and reproducible potentiometric response in the real seawater. The raw data from the carbonate-selective electrode were used to calculate the activities of carbonate at given pH values and converted to corresponding TCO_2 values using the dissociation constants of carbonic acid.^{8,23} The level of TCO_2 in Yellow Sea water determined in this manner was 1.94 ± 0.03 ($n = 15$) mmol/kg-soln.

To validate the results obtained with carbonate-selective electrode, TCO_2 level was measured using the Severinghaus-type CO_2 sensor. Since the mole fraction of $\text{CO}_{2(\text{aq})}$ in alkaline seawater is very small (<1%), the direct use of the CO_2 gas sensor in seawater analysis yielded very poor results. Thus, the seawater sample was treated with 0.2 M citric acid buffer (pH 5.0) in equal volume ratio prior to the measurement. The Severinghaus-type CO_2 sensor also provides stable and reproducible results in an acidic condition. The TCO_2 level determined from this measurement was 1.93 ± 0.01 ($n = 3$). Potentiometric titration method, one of the well-established analytical procedures for oceanic TCO_2 measurement, was also employed to compare the results of seawater analysis obtained with ISEs.²⁵ The level of TCO_2 calculated from the potentiometric titration was 1.95 ± 0.04 ($n = 8$). The TCO_2 levels determined using three different methods are listed in Table 1; the values are in very close range within instrumental error, which confirms that the analytical procedure based on the carbonate-selective electrode is sufficiently accurate to use in the field.

CONCLUSION

A new carbonate-selective electrode based on the neutral carrier deoxy-3,12-bis(TFAB)CA was prepared, and its potentiometric properties were examined in buffered electrolytes (0.1 M Tris-H₂SO₄, pH 8.6 and 8.0) and artificial seawater. It was found that the electrode provides sufficiently high carbonate selectivity over chloride and other anions present in seawater. Thus, we examined the possibility of measuring oceanic carbon dioxide with ISE method. The TCO₂ level in Yellow Sea water was measured with the deoxy-3,12-bis(TFAB)CA-based electrode, Severinghaus-type CO₂ sensor, and the traditional potentiometric titration methods. The results showed that the carbonate-selective electrode provides accurate TCO₂ determination comparable to that obtainable with the other two methods. Of the three methods, however, the analytical procedure based on the carbonate-selective

electrode provides distinctive advantages: it does not require sample pretreatment and extra reagents other than the standard calibration solutions, while providing direct and immediate results.

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