RESPONSE PROPERTIES, APPLICATIONS AND LIMITATIONS OF CARBONATE-SELECTIVE POLYMER MEMBRANE ELECTRODES

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SUMMARY

The preparation and response characteristics of a carbonate-selective polymer membrane electrode are reported. The electrode is prepared by incorporating Aliquat 336, trifluoroacetyl-*p*-butylbenzene and di-2-ethylhexyl sebacate or dioctyl phthalate in a poly(vinylchloride) membrane matrix. The effect of membrane composition and electrode response in various buffer systems are examined. Under buffer conditions appropriate for practical measurements, potentiometric data yield the following selectivity pattern: $ClO_4^- =$ salicylate > total carbon dioxide species > $I^- > NO_3^- >$ acetate > $Cl^- > Br^-$. The electrode can be readily fabricated in tubular form and utilized within a very simple flow-injection arrangement to determine total carbon dioxide species. The possible applications of the electrode to serum CO_2 measurements as well as within newly devised gas-sensing arrangements for dissolved CO_2 are also examined.

The accurate and rapid determination of total carbon dioxide species (e.g., CO_2, hydrogencarbonate, and carbonate) in physiological, industrial, and environmental samples presents a formidable challenge. At present, total CO_2 is most often determined with a Severinghaus-type potentiometric gas sensor [1] after the sample has been acidified to pH < 5.5. In such systems, measurements are based on the diffusion of CO_2 through a silicone rubber membrane into a thin film of hydrogencarbonate solution in contact with a glass pH electrode. A change in pH results within the aqueous film as complete equilibration of the gas across the membrane is achieved. While widely employed, the Severinghaus design suffers from limitations because of its slow response times, the fragile and costly nature of the required flat-bottom pH glass electrode, and the large response of the sensor to volatile as well as some less volatile organic acids [2].

In view of these limitations, there have been numerous attempts to prepare alternative potentiometric devices capable of detecting total CO_2 species in solution. These devices include membranes based on solid ion-exchange resins sensitive to hydrogencarbonate [3] and pseudo "bicarbonate"-responsive electrodes based on dual pH sensitive/CO_2 permeable polymer membranes [4, 5]. The former lacked selectivity while the latter were really gas-sensing electrodes in which response to hydrogencarbonate occurred as equilibrium levels of CO_2 (in the hydrogencarbonate solutions) permeated a polymeric

pH-responsive membrane, altering the internal membrane potential of the sensor (i.e., changed pH at the internal surface of the membrane). Another "bicarbonate" electrode, based on a liquid membrane with a fluorinated ketone anion-exchanger was patented by Corning [6]. It was subsequently demonstrated by Herman and Rechnitz [7, 8] that this electrode (utilizing Aliquat 336 in trifluoroacetyl-p-butylbenzene as the active membrane phase) was really selective for carbonate, not hydrogencarbonate. Indeed, these workers were able to use this liquid membrane probe to determine total CO_2 in blood by measuring equilibrium amounts of carbonate at pH 8.4 [9]. Kodak Corporation now utilizes a polymer form of this membrane to measure serum CO_2 within their new Ektachem clinical analyzer [10], but no literature report has appeared describing the preparation and properties of such a membrane.

The purpose of this paper is to report our findings on the preparation, optimization, and response characteristics of a carbonate-selective polymeric membrane electrode. In addition, a novel tubular form of the electrode is described and utilized in a simple flow-injection arrangement for the determination of total CO_2. Limitations on the use of this membrane electrode system for direct blood CO_2 measurements are discussed. Finally, the concept of incorporating this polymer membrane electrode within a newly devised gas-sensing arrangement, highly selective for CO_2, is also examined.

EXPERIMENTAL

Apparatus

All static and flow-injection potentiometric measurements were made with a Corning Model 12 pH/mV meter used in conjunction with a Heath-Schlumberger Model 204 strip-chart recorder. All measurements were made vs. a saturated calomel reference electrode at room temperature. An Orion Model 92-00 liquid-membrane electrode body was used to evaluate the static response of carbonate-selective polymer membranes.

A schematic diagram of the carbonate electrode-based flow-injection system is shown in Fig. 1. The system consists of a Rainin-Rabbit peristaltic pump, a Rheodyne 4-way rotary injection valve (with 100-μl sample loop), 50 cm of 1.14-mm i.d. polyethylene tubing coiled in 1-inch loops, and a tubular carbonate polymer membrane electrode.

Reagents

All chemicals were of the purest grade available. Standard solutions and reagent buffers were prepared with distilled—deionized water. Most experiments were carried out with either a 0.05 M or 0.10 M tris-(hydroxymethyl)-aminomethane—hydrogen sulfate (Tris—SO_4) buffer, pH 8.75, as the sample or diluent reagent.

Trifluoroacetyl-p-butylbenzene (TFBB) was synthesized as described previously [8]. Aliquat 336 (tricaprylylmethylammonium chloride) was
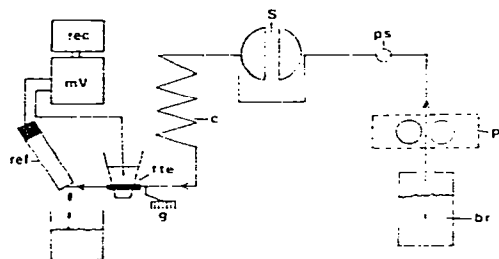
Fig. 1. Schematic diagram of the polymer carbonate electrode-based flow-injection system: (fte) tubular flow-through carbonate electrode; (g) electrical ground; (c) coiled polyethylene tubing; (s) sample injection valve; (ps) pulse suppressor; (p) peristaltic pump; (br) buffer reservoir.

obtained from Aldrich Chemical Co. Dioctyl phthalate and dioctyl sebacate were Kodak products, while di-2-ethylhexyl sebacate was obtained from ICN Pharmaceuticals.

Preparation and evaluation of membrane electrodes and gas sensor

For static electrode studies, the carbonate-selective membrane was prepared as follows. Poly(vinylchloride) (55 mg), plasticizer (50 μl), TFBB (50 μl) and THF (1 ml) were mixed thoroughly and the resulting solution was poured into a glass ring (1-inch diameter) placed on top of a glass slide. After the solvent had evaporated, the membrane was peeled from the slide and smaller round discs were cut out (3-mm diameter). Such a piece was placed in the end of an Orion liquid electrode body and secured in place by tightening the outer cap. The electrode was filled with an internal solution of 0.01 M $NaHCO_3$—0.01 M NaCl before testing.

For evaluation within the gas sensor arrangement, a small piece of the above membrane was affixed to the end of a plastic pipet—tygon tubing assembly as described previously for an ammonium-selective membrane [11, 12]. The rest of the gas sensor was also assembled in an analogous manner to the earlier ammonia probe [12] except that a silicone rubber membrane was used as the outer gas-permeable material.

A tubular flow-through carbonate electrode was prepared with a slightly different membrane composition. Instead of 55 mg of PVC, 25 mg was used in the casting solution. The electrode was made in a 0.89-mm i.d. piece of tygon tubing by methods recently described for tubular ammonium electrodes [13]. The electrode was encased in an appropriate housing into which the internal reference solution (0.01 M $NaHCO_3$—0.01 M NaCl) and a Ag/AgCl reference wire were placed.

The static electrode potentiometric response and selectivity characteristics were evaluated by making standard additions of 0.1 M $NaHCO_3$, or interferents, to 25 ml of well stirred Tris—SO_4 buffer. The pH of the buffer was simultaneously monitored with a glass electrode to determine whether

responses observed were a result of pH changes caused by the addition of test reagents (a pH change shifts the CO_3^{2-}/HCO_3^- equilibrium and the electrode responds to OH^-). For evaluation of the gas sensor, CO_2 was formed by standard addition of $NaHCO_3$ to a 0.2 M citrate buffer, pH 4.50.

RESULTS AND DISCUSSION

In preliminary efforts to utilize the liquid-membrane components described by Herman and Rechnitz [7] within a polymer matrix, it was found that TFBB was not a suitable plasticizer for PVC type membranes. Consequently, a mixture of that solvent along with more traditional plasticizers must be used in order to make functioning electrodes. Several plasticizers were tested and the response properties of the electrode were found to vary somewhat, depending on the plasticizer utilized. In general, these effects were not dramatic; however, optimal response with regard to slope was obtained with di-2-ethylhexyl sebacate and dioctyl phthalate. The ratio of plasticizer to solvent-exchanger, and the amount of PVC within the membrane were also studied. Again, no significant trend was observed, although a membrane composed of 23% plasticizer, 23%—4% Aliquat 336 in TFBB and 54% PVC consistently yielded optimal response.

Characteristics of the electrode

A considerable effort was made to determine the best buffer composition to use for practical evaluation of the electrode. Herman and Rechnitz [9] reported the use of a Tris—HCl buffer, pH 8.40, for automated serum CO_2 measurements using a liquid-membrane carbonate electrode. For the polymer membrane electrode, several buffer systems (e.g., Tris, 2-amino-2-methyl-1,3-propane-diol, 2-amino-2-methyl-1-propanol) were studied to find the one which yielded optimal response to total CO_2 species. In addition, the counter-ion was varied within the buffers. For example, Fig. 2 shows the response of the static carbonate polymer electrode to total carbonate—hydrogencarbonate species in a series of 0.05 M Tris—X buffers, all at pH 9.0. It can be seen that Tris—SO_4 offers the widest dynamic range and the best slope (typically 25—27 mV/decade). Clearly, the data from this study reflect the innate selectivity of the membrane with respect to various buffer anions. After it had been shown that Tris—SO_4 was the most useful working buffer for quantitative purposes, a more complete selectivity study was done with this buffer solution as a constant background. Figure 3 shows the response of the carbonate electrode to total CO_2 species (i.e., carbonate and hydrogencarbonate) and to other anions in 0.1 M Tris—SO_4, pH 8.75. It can be seen that the electrode responds logarithmically to total CO_2 species between 7×10^{-4} and 1×10^{-2} M, although useful response is observed to 10^{-4} M. It should be realized that at pH 8.75, only 2.4% of the total CO_2 species is carbonate and thus the membrane is far more selective for carbonate than it appears from Fig. 3. However, because the electrode also has a large Nernstian
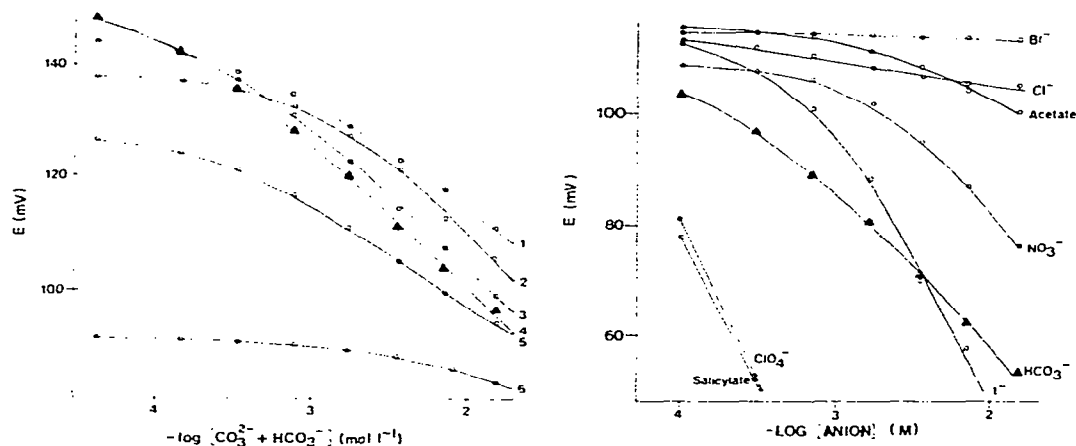
Fig. 2. Response of static carbonate polymer-membrane electrode to total CO_2 (predominately carbonate and hydrogencarbonate) in various 0.05 M Tris—X buffers, pH 9.0: (1) Tris—HCl; (2) Tris—citric acid; (3) Tris—HBr; (4) Tris—H_2SO_4; (5) Tris—HF; (6) Tris—HI.

Fig. 3. Potentiometric response of polymer carbonate electrode to various anions in a background of 0.1 M Tris—SO_4, pH 8.75.

response to hydroxide ion, increasing the working pH would result in poorer detection limits toward total CO_2 species. Indeed, pH 8.75 was found to be a good compromise for practical measurement purposes and, therefore, Fig. 3 reflects the practical selectivity relative to total CO_2 measurements (not relative only to carbonate). Figure 3 indicates that perchlorate and salicylate are the major interferences and that the selectivity order of the electrode is as follows: salicylate = perchlorate > total CO_2 species ⩾ I^- > NO_3^- > acetate > Cl^- > Br^-.

For the data shown in Figs. 2 and 3, a 0.01 M $NaHCO_3$—0.01 M NaCl solution was used as the internal reference solution. Response times were typically 20 s—1 min for complete equilibration. The effect of using buffered internal reference solutions was examined with the aim of avoiding any effect that CO_2 diffusion through the PVC membrane [4, 5] might have on the equilibration time and slope of the electrode (e.g., CO_2 diffusion could alter the pH of the internal solution and continuously change the $E°$ of the electrode). The following buffers, all containing 10^{-2} M NaCl, were evaluated: 0.1 M Tris—SO_4, pH 8.75; 0.1 M phosphate, pH 7.00; 0.1 M citrate, pH 5.50. Although shifts in the initial potentials were observed, the electrode performance for all of these internal buffers was essentially the same as when the unbuffered internal solution was used. This suggests that free CO_2 gas levels are so low when the sample solution is at pH 8.75 (0.4% of total CO_2 species), that no concern need be given to the CO_2 diffusion problem, at least in the 10^{-4}—10^{-2} M total CO_2 working range.

Flow-injection system

In an effort to utilize the electrode for rapid and accurate total CO_2 determinations, it was judged desirable to incorporate the polymer membrane electrode into a flow-injection system. When a novel tubular electrode assembly [14] was used with a flow-injection system (Fig. 1) and a 0.1 M Tris—SO_4 (pH 8.75) diluent stream, the potentiometric recording shown in Fig. 4 was obtained. These data were recorded by injecting $NaHCO_3$ standards from the 100-μl injection value. Typically, 40—50 samples per hour can be handled with good reproducibility ($\leqslant \pm 0.8$ mV). In this flowing system, the electrode had a slightly lower slope, typically 23—25 mV/decade between 5×10^{-3} and 1×10^{-1} M total CO_2 species. The shift in calibration plots when compared to Figs. 2 and 3 reflects the internal dilution factor within the flow-injection system. In this regard, because exact pH adjustment of the sample is critical for accurate total CO_2 measurements, greater dilution within the system is required (achieved by using tubing of wider diameter and greater length).

In attempts to utilize the above flow-injection system for serum CO_2 measurements, it was found that large positive errors resulted (using pre-assayed commercial control serum). This was apparently due to the presence of salicylate anions in the control serum (at 3.65×10^{-4} M [15]). Normal salicylate levels in blood are typically less than 1.0×10^{-4} M [16], but therapeutic levels for aspirin users are approximately 1.5×10^{-3} M [16]. It is clear from Fig. 3 that any salicylate greater than normal levels will cause substantial positive errors in total CO_2 measurements via the polymer carbonate electrode-based methods. The carbonate-responsive polymer membrane utilized by Kodak Corporation in their new instrument must also suffer salicylate response, because a recent patent [17] describes a buffer overcoat layer which is supposed to eliminate organic anion interferences.
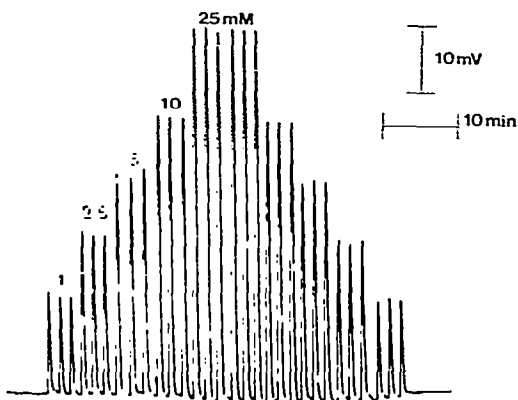

Fig. 4. Typical strip-chart recording and reproducibility obtained with carbonate electrode-based flow-injection system. Carrier flow rate, 2.0 ml min^{-1}; 100-μl injections.

Because the Kodak system involves a single use, disposable, static membrane electrode arrangement, such a solution to this problem is feasible. However, such an approach could not be utilized in a flowing arrangement in which the membrane electrode is continuously being reused.

To improve the selectivity of the static carbonate polymer membrane, the feasibility of utilizing the electrode as an internal sensing element in a conventional total CO_2 gas sensing arrangement was examined. The concept of using polymer electrodes as inner sensing elements was recently introduced via a new ammonia sensor [11]. Figure 5 illustrates the device used in this study. When a 0.1 M Tris—SO_4 buffer, pH 8.75, served as the internal electrolyte, very small potentiometric responses were obtained as standard $NaHCO_3$ was added to a sample solution of pH 4.50. Indeed, for such an experiment, the predominant response was in the positive potential direction. This was because CO_2 diffusion across the outer gas-permeable membrane caused a pH change within the thin film of buffer at the sensor tip. Such an effect is enhanced by the relatively large pH difference between the sample solution and the internal buffer solution (i.e., large buffer trap effect). When the internal buffer solution was replaced with stronger buffer solution, e.g., 0.5 M Tris—SO_4, pH 8.75, the calibration plot shown in Fig. 6 was obtained. Response times were typically 2 min; however, the slope was lower than expected (20 mV/decade) and the logarithmic range was quite narrow. Again, at total CO_2 levels greater than 10^{-3} M, the potentiometric response reverses because of a lowering of the pH in the buffer film (reduced carbonate ion levels in film). To overcome this problem, it would be desirable
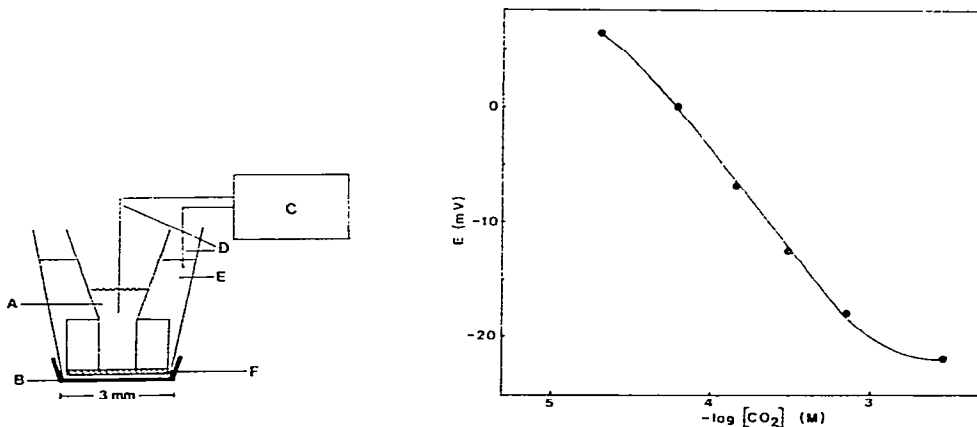

Fig. 5. Schematic diagram of polymer electrode-based carbon dioxide-responsive gas sensor: (A) 0.01 M $NaHCO_3$—0.01 NaCl solution; (B) silicone rubber membrane; (C) pH/mV meter; (D) Ag/AgCl electrodes; (E) Tris—SO_4 buffer; (F) poly(vinylchloride) carbonate-selective membrane.

Fig. 6. Calibration curve for carbonate electrode-based potentiometric CO_2 gas sensor.

to utilize a hydrogencarbonate-responsive internal sensing element. This would allow the use of a lower pH internal buffer and thus would reduce the pH changes caused by the buffer trap effect. Work on this concept is currently underway.

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