SULFITE-SENSITIVE SOLVENT/POLYMERIC-MEMBRANE ELECTRODE BASED ON BIS(DIETHYLDITHIO-CARBAMATO)MERCURY(II)

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SUMMARY

A new solvent/polymeric-membrane electrode which exhibits significant potentiometric response toward sulfite ion in the 1×10^{-6}–1×10^{-3} M range is described. The membrane is prepared by incorporation of neutral bis(diethyldithiocarbamato)mercury(II) in a thin film of plasticized poly(vinyl chloride). In sharp contrast to classical Hofmeister behavior, the resulting membrane displays little or no response to a wide range of anions (log $K_{i,j}^{pot} \leqslant -4$, i being sulfite) including sulfate, nitrate, nitrite, chloride, perchlorate, salicylate, and alkylsulfonates. Bromide and thiocyanate are moderate interferents, while significant response to iodide, thiosulfate, and sulfide is observed. These selectivity data, along with other response characteristics of the membrane, are used to postulate the mechanism by which the electrode responds to sulfite. Preliminary studies demonstrate that the electrode can be used in conjunction with an outer gas-permeable membrane for highly selective detection of total sulfite species in the form of sulfur dioxide.

The development of solvent/polymeric-membrane electrodes with high selectivity for given anions remains a formidable challenge. Membranes based on dissociated ion-exchangers such as lipophilic quaternary ammonium or phosphonium species always display classical Hofmeister behavior in which the more hydrophobic anions are preferred (e.g., lipophilic organic anions, perchlorate, thiocyanate, etc.) [1,2]. Deviation from this behavior can only be achieved if the active component of the membrane functions as an associated charged or neutral carrier molecule [3,4]. Recent studies have shown that certain organometallic compounds (including organotin species [5,6], derivatives of vitamin B_{12} [7,8], and manganese(III) and tin(IV) porphyrins [9–11]), when used in plasticized poly(vinyl chloride) matrices, yield potentiometric anion-selectivity sequences which are markedly different from the Hofmeister pattern. Apparently, these deviations arise from the direct interaction between analyte anions and the metal center of the membrane-active species. The work

reported here extends this concept with the development of a new sulfite-sensitive membrane electrode based on the mercury(II) complex of diethyldithiocarbamate, $Hg(DDC)_2$.

A truly selective sulfite/hydrogen sulfite sensor would have a wide range of analytical applications, including the direct determination of these antioxidants in food and beverages. Recently, the control of sulfite levels in dietary products has been the subject of concern in connection with the adverse health effects resulting from the ingestion of excess of sulfite [12,13]. In addition, a sulfite/hydrogen sulfite-responsive electrode, even with less than perfect sulfite selectivity, could prove extremely valuable in the design of new sulfur dioxide-selective gas detectors, using sensing configurations analogous to those previously described for detecting ammonia [14–16], carbon dioxide [17], and oxides of nitrogen [18].

It is well known that mercury(II) interacts strongly with reduced forms of sulfur, including sulfite [19]. Indeed, this interaction forms the basis for the standard West–Gaeke procedure used to trap and subsequently determine atmospheric sulfur dioxide [20]. Thus, the goal of the present work was to take advantage of this natural affinity between mercury(II) and sulfur(IV) to design a new membrane electrode for detecting sulfite and/or hydrogen sulfite ions. In preliminary studies, several mercury(II) compounds were examined [diphenylmercury, mercury(II)-diphenylthiocarbazone, and $Hg(DDC)_2$]. Of these, $Hg(DDC)_2$ proved most suitable for incorporation into polymeric matrices, yielding membranes with significant sulfite response and selectivity.

EXPERIMENTAL

Apparatus

Membranes were mounted in Philips IS-561 electrode bodies (Glasblaserei Moller, Zürich) for testing. Potentiometric measurements were made with a Fisher Model 620 mV/pH meter and recorded on a Fisher Recordall Series 5000 strip-chart recorder. For gas-dialysis experiments, a sheet of Gore-Tex (W.L. Gore & Associates, Elkton, MD) microporous teflon (0.2-μm pore size) was held in a dialysis block as reported previously [15,18]. Recipient buffer was pumped through the system with an Ismatec (Zürich) variable-speed peristaltic pump through plastic tubing. Polyethylene tubing was used wherever possible to minimize diffusion of oxygen into the flow streams; elsewhere, PVC tubing was used.

The electrochemical cell used for the experiments reported here was as follows: SCE reference ‖ buffered sample solution | membrane | 0.1 M NaCl, AgCl(s) | Ag wire.

For static-probe measurements, the sample solution was contained in a jacketed beaker, thermostated at $25 \pm 0.1°C$.

Reagents

All chemicals used were reagent grade. Diethyldithiocarbamate (sodium salt, trihydrate), dibutyl phthalate, and diphenylmercury(II) were obtained from Aldrich Chemical Co. Chromatographic grade poly(vinyl chloride) (PVC; Polysciences, Warrington, PA) was used for membrane construction. 2-(*N*-Morpholino)ethanesulfonic acid (MES) was obtained from Sigma Chemical Co. Tetrahydrofuran (THF) for membrane castings was distilled before use. Water was deionized to $\geqslant 15$ MΩ cm.

Preparation of bis(diethyldithiocarbamato)mercury(II). Two equivalents of solid sodium diethyldithiocarbamate were added to a separatory funnel containing 100 ml of 0.1 M NaHCO$_3$ and 100 ml of chloroform. With swirling, one equivalent of Hg^{2+} (from HgO in dilute nitric acid solution) was added slowly, forming a yellow precipitate. Additional Hg^{2+} solution was then added dropwise until rust-colored HgO appeared (to signal excess of Hg^{2+}). The yellow precipitate was extracted into the chloroform layer; following three water washes, the chloroform was rotary-evaporated to isolate pale yellow crystals. The crystals were washed twice with methanol and dried under vacuum. Yields were typically 70–80%; m.p. 137–139°C (lit. 138–139°C [21]). Calculated for C$_{10}$H$_{20}$HgN$_2$S$_4$: 24.2% C, 4.1% H, 5.6% N; found (by Oneida Laboratories, Whitesboro, NY): 24.2% C, 4.0% H, 5.6% N. The infrared spectrum (KBr pellet) matched published data [22]. The zinc(II) complex of DDC was prepared in similar fashion.

Procedures

Preparation of membrane electrode. Solvent/polymeric membranes incorporating the carrier were typically made with the following formula: 5 mg of Hg(DDC)$_2$ (1.8% w/w), 200 μl of plasticizer (usually dibutyl phthalate, DBP; 74.8% w/w), and 65 mg of PVC (23.4% w/w). This mixture was dissolved in 1200 μl of freshly distilled THF, and cast in 22-mm i.d. glass rings on a glass plate. After drying (usually overnight), individual membranes (5-mm diameter) were cut from this larger piece and mounted in electrode bodies for testing.

Evaluation of membrane response and selectivity. Sulfite standards were prepared by dissolving sufficient anhydrous sodium sulfite in water containing 0.1% (v/v) glycerol to inhibit oxidation [23], to make 1 M sulfite; 10^{-1}–10^{-4} M sulfite standards were prepared by serial dilution (with aqueous 0.1% glycerol) of the 1 M stock standard. Potentiometric measurements were made by immersing the electrodes in 50 ml of buffer (usually 10 mM phosphate pH 10, although borate and carbonate buffers were also studied); after a baseline potential was established, microliter-volume additions of the prepared standards were made to generate sulfite ion concentrations in the 10^{-7}–3×10^{-2} M range. Activities of sulfite were calculated based on the extended Debye–Hückel equation.

For selectivity studies, the separate-solutions method was used in a back-

ground electrolyte of 10 mM phosphate buffer, pH 10.0. The EMF of the cell was recorded as a function of various anion (sodium salts) activities generated as above for sulfite measurements. The pH sensitivity of the membrane was studied in a "universal" pH buffer, consisting of boric acid, citric acid, and sodium phosphate (monobasic) (10 mM each), adjusted to various pH values with 1 M sodium hydroxide. The pH of this test solution was monitored simultaneously with a combination glass-membrane pH electrode.

Sulfur dioxide-sensing arrangement. The sulfite electrode was fitted with a home-made flow-through cap and placed (along with a flow-through SCE reference) downstream from a membrane dialyzer, in a manner analogous to that described earlier [18] for NO_x detection. A 0.1 M MES buffer, pH 6.0, was used as the recipient solution (flow rate 0.6 ml min^{-1}). Aqueous sulfite standards (10^{-6}–10^{-2} M) were acidified in the flow stream by 1:1 dilution with 0.1 M phosphoric acid to generate dissolved sulfur dioxide in proportion to the total sulfite present.

RESULTS AND DISCUSSION

Response characteristics of PVC membranes doped with Hg(DDC)$_2$.

Three plasticizers were tested during the development of the sulfite-sensitive membrane: dibutyl phthalate (DBP), o-nitrophenyl octyl ether (o-NPOE), and dibutyl sebacate (DBS). The Hg(DDC)$_2$ complex is soluble in the aromatic plasticizers DBP and o-NPOE, but exhibits no observable solubility in DBS. Sulfite response can be obtained from membranes plasticized with either DBP or o-NPOE; for this work, DBP was chosen over o-NPOE because of the high cost and instability of the latter.

Figure 1 shows the sensitivity to sulfite-ion activity exhibited by solvent/ polymeric membranes containing various amounts of Hg(DDC)$_2$. The calibrations were done in 10 mM phosphate buffer, pH 10, where nearly 100% of the added sulfite is in the divalent form. As shown, response is dependent upon the proportion of active compound contained in the membrane formulation. For optimal performance, 1–2% (w/w) Hg(DDC)$_2$ was required. When less carrier is used, the sulfite response is diminished significantly (see Fig. 1). The content of active compound in the membrane cannot be increased beyond ca. 2.5% (w/w), because the solubility of the carrier in DBP is then exceeded.

The Hg(DDC)$_2$-based membrane displays remarkable selectivity for sulfite over most common anions. Table 1 lists the ions tested which elicited little or no potentiometric response ($K_{i,j}^{pot} \leqslant 10^{-4}$). Virtually all of these ions are more lipophilic than sulfite, and would be expected to interfere seriously with classical anion-exchanger type membranes. Major interferents include iodide, bromide, thiocyanate, and thiosulfate (Table 1). Sulfide is by far the most significant interferent: micromolar amounts of this ion can render the membrane inoperative and must therefore be avoided.
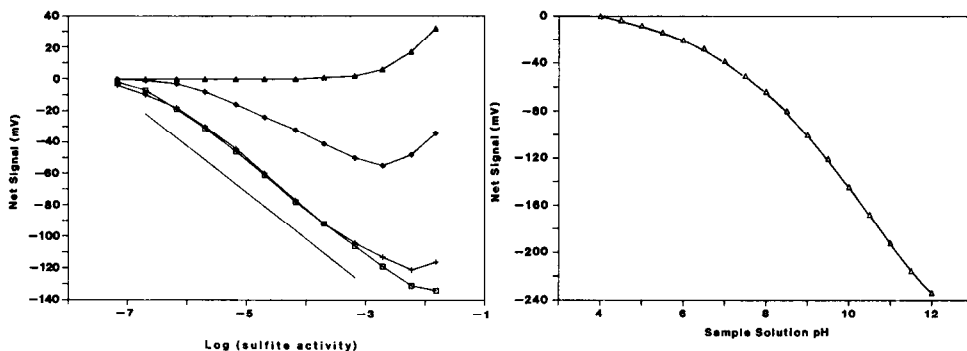
Fig. 1. Potentiometric response of Hg(DDC)$_2$-based membranes to additions of sodium sulfite in 10 mM phosphate buffer, pH 10.0. Membranes contained various amounts of Hg(DCC)$_2$: (□) 1.8, (+) 1.1, (◇) 0.4, and (△) 0.0% (w/w). The straight line represents the theoretical bivalent anion response.

Fig. 2. Response of Hg(DDC)$_2$-based membrane with 1.8% (w/w) Hg(DDC)$_2$ to sample pH in the absence of sulfite.

TABLE 1

Potentiometric selectivity coefficients of Hg(DDC)$_2$-based membrane[a]

Anion	log $K_{i,j}^{pot}$
Cl$^-$, acetate, citrate, ClO$_4^-$, salicyclate, HCO$_3^-$/CO$_3^{2-}$, RSO$_3^-$, NO$_2^-$, NO$_3^-$, OCN$^-$, SO$_4^{2-}$	$\leqslant -4$
Br$^-$, SCN$^-$	0
S$_2$O$_3^{2-}$	0.5
I$^-$	7

[a]Selectivity coefficients measured via the separate-solution, matched-potential method in 10 mM phosphate buffer, pH 10.0; the primary ion i is sulfite.

Transition and post-transition metals are well known for their tendency to form oxides and hydroxides at moderate or high pH. This property lends pH sensitivity to anion-selective membranes which are based on organometallic complexes containing these metals, e.g., tin or manganese porphyrins [9,10]. As expected, the Hg(DDC)$_2$-based membrane also exhibits this behavior. The pH dependence of the membrane potential was studied in "universal" buffer as described in the experimental section (Fig. 2). In acidic solution, little pH response is observed. At higher hydroxide activity, where sulfite or hydrogen sulfite measurements must be made, a buffered sample solution is required to prevent signal drift.

Buffers other than phosphate were also tested to determine whether background levels of di- and tri-basic phosphate anions limit the detection capa-

bilities of the membrane. Figure 3 shows the sulfite calibrations obtained in 10 mM phosphate, carbonate, and borate buffers (all pH 10). Borate seems to exert a slight deleterious effect on the membrane performance (decreased slope and linear response range). The response of the membrane in phosphate and carbonate buffers is quite similar. Not evident from these curves is the fact that electrode response time in carbonate buffer is somewhat longer than in phosphate. Thus, the latter is recommended for optimal dynamic behavior.

The membrane was also tested at lower pH. In MES buffer, pH 6.0, for example, a calibration is obtained with a maximum slope near 50 mV/decade and a detection limit of ca. 1 μM (Fig. 3). This indicates that the membrane is also responsive to hydrogen sulfite (HSO_3^-). This sensitivity can be used to advantage in a more selective flow-through sulfur dioxide gas-sensing arrangement (see below).

The response time of the $Hg(DDC)_2$-based membrane depends mainly on the direction of the change in analyte activity, the activity range being measured, and the concentration of the background buffer. For example, the equilibrium step changes in potential depicted in Fig. 1, moving from lower to higher sulfite activity, can be measured in less than 2 min in 10 mM phosphate buffer. In 100 mM buffer, this response time is increased. (As mentioned above, the response is also lower in carbonate than in phosphate buffer.) For changes in the reverse direction, the response is slightly slower in the mM region (2–4 min) and significantly slower ($\geqslant$ 20 min) at micromolar sulfite activities.
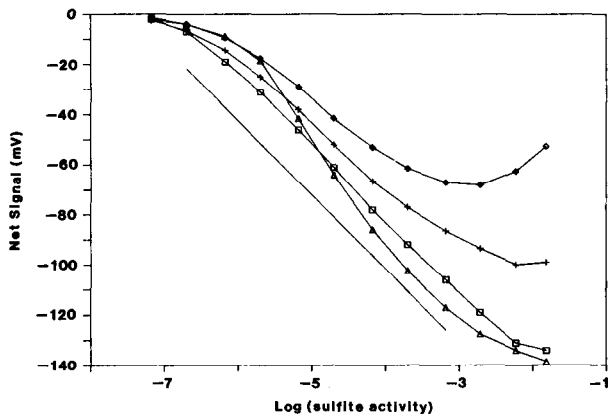

Fig. 3. Sulfite response of $Hg(DDC)_2$-based membrane with 1.8% (w/w) $Hg(DDC)_2$ in different buffers: ($\square$) 10 mM phosphate, pH 10.0; (+) 10 mM carbonate, pH 10.0; ($\Diamond$) 10 mM borate, pH 10.0; ($\triangle$) 0.1 M MES, pH 6.0. The curve showing response in MES buffer is plotted vs. total HSO_3^- + SO_3^{2-} concentration, not activity. The straight line represents the theoretical bivalent anion response.

Mechanism of membrane response

The coordinative properties of DDC have been applied to potentiometry in the past. Graphite rods impregnated with copper or silver DDC are sensitive to DDC⁻ ion in solution [24]. Lead(II)-selective electrodes based on $Pb(DDC)_2$ incorporated in PVC [25] or coated onto a lead wire [26] can measure lead(II) down to micromolar levels. Membranes sensitive to copper(II) have been developed, based upon two covalently linked DDC ligands which, together, serve as a coordinative binder for the metal ion [27]. Each of these electrodes operates by an analyte-exchange process: either the metal ion or the DDC ligand is exchanged between the membrane and sample phases to provide the potentiometric signal.

The $Hg(DDC)_2$ ionophore reported here appears to operate via a different principle. Because of the strength of its Hg–S bonds, it is believed that the $Hg(DDC)_2$ remains essentially intact within the membrane phase, exchanging neither mercury(II) nor DDC⁻ with the aqueous solution. The DDC ligands serve as an organic "anchor", keeping the mercury(II) in the organic phase where it can serve as a coordinating site for sulfite ions. In this scheme, two slightly different response mechanisms are possible (see Fig. 4). An incoming sulfite ion (or interfering iodide, thiocyanate, etc.) can either (A) displace a coordinated thiocarbonyl sulfur from the mercury(II), or (B) simply add on as a fifth ligand. Based on the tendency of mercury(II) to form four-coordinate complexes, and on previously reported studies of the $Hg(DDC)_2$ molecule [28] which suggest weaker interaction between thiocarbonyl sulfur atoms and the mercury(II) (e.g., based on bond lengths), mechanism (A) of Fig. 4 is the most likely. It should be noted that, for either mechanism, the $Hg(DDC)_2$ complex would be serving as a neutral-carrier type ionophore.

The fact that metal-DCC complexes have been used previously [25–27] to devise metal-ion sensors suggests that the sulfite-sensitive electrode described here may be subject to interferences by transition metal ions which form strong
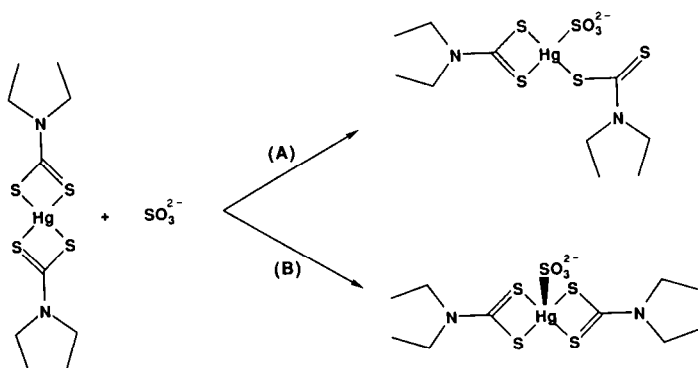

Fig. 4. Postulated coordination schemes of $Hg(DDC)_2$ with sulfite.

complexes with the DDC ligand. However, no potentiometric response was observed when lead (II), silver (I), mercury (II), or copper (II) ions were added (up to 10 mM) to phosphate-buffered test solutions, pH 10.0 (with or without glycerol). Clearly, the levels of free metal ions in the pH 10.0 sample solution are too low to be detected because of formation of metal-hydroxide species under these alkaline conditions.

The conclusion that mercury (II) is instrumental in the response properties of this membrane toward sulfite is based on three facts. First, the observed selectivity pattern matches that which might be expected from a mercury (II)-based system. Mercury (II), being a "soft" acid, can be expected to complex the "soft-base" anions most strongly [29]. Secondly, when $Zn(DDC)_2$ is used in the membrane in place of $Hg(DDC)_2$, no sulfite-ion response is observed. Thirdly, other organic Hg(II) species can be incorporated into membranes to yield sulfite sensitivity. In this work, diphenylmercury (II) was also tested as a sulfite ionophore. Although inferior in detection limit and signal stability to $Hg(DDC)_2$, such membranes do exhibit response to sub-millimolar levels of sulfite.

Sulfur dioxide gas-sensing arrangement

Although the sensitivity of the $Hg(DDC)_2$ membrane to sulfite activity is excellent, its lack of selectivity over iodide, bromide, and reduced-sulfur anions could prohibit its use as a direct sulfite sensor in complex samples. This selectivity problem can be overcome by the use of a sulfur dioxide gas-sensing arrangement analogous to those reported previously for ammonia [15], carbon dioxide [17], and oxides of nitrogen [18]. The requisite chemistry and flow arrangement are depicted in Fig. 5. A sample stream containing sulfite/hydrogen sulfite is acidified to pH <2 and passed through a gas-dialysis chamber. The sulfur dioxide produced diffuses through a gas-permeable membrane into a recipient buffer at pH 6, where it re-dissolves as a hydrogen sulfite/sulfite mixture. The recipient solution then flows past an $Hg(DDC)_2$ membrane (with SCE reference), which measures the collected sulfite/hydrogen sulfite.

As shown in Fig. 6, a dramatic improvement in selectivity is obtained by using this approach. Sulfite ion species in the sample stream can be measured because of the high vapor pressure of aqueous sulfur dioxide. However, iodide and bromide, even when acidified, do not generate sufficient gaseous HI or HBr to produce significant levels of interferent anions in the recipient stream. Thiosulfate can be expected to decompose slightly in acidic solution to form hydrogen sulfide and sulfur dioxide; it therefore does interfere somewhat, although much less severely than in direct-probe measurements (Table 1). The interference caused by thiocyanate is also greatly diminished, although not completely removed. Overall, by using the gas-sensing arrangement, apparent selectivity coefficients for these anion species are reduced to $\leqslant 10^{-4}$.

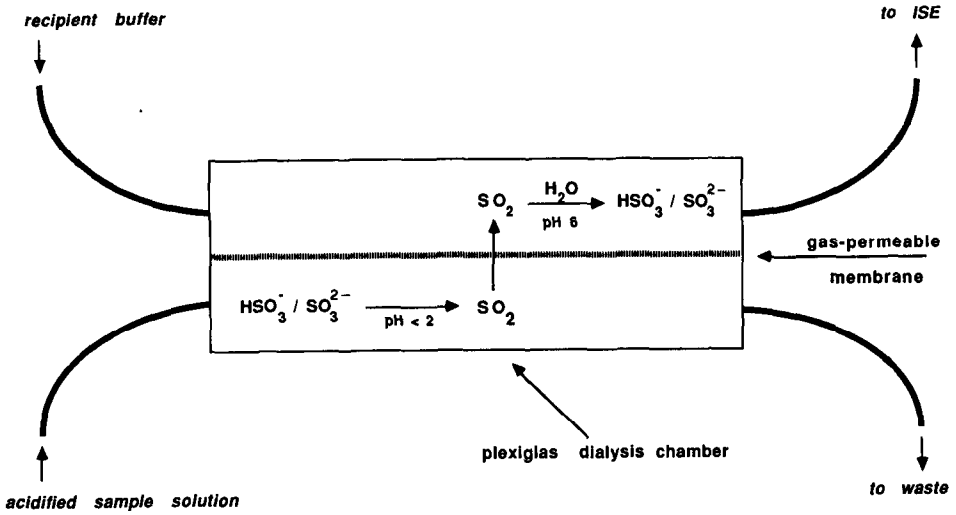In principle, any buffer suitable for direct-probe measurements may be used

Fig. 5. Schematic diagram of flow-through SO_2 gas-sensing system based on a sulfite-sensitive membrane electrode.
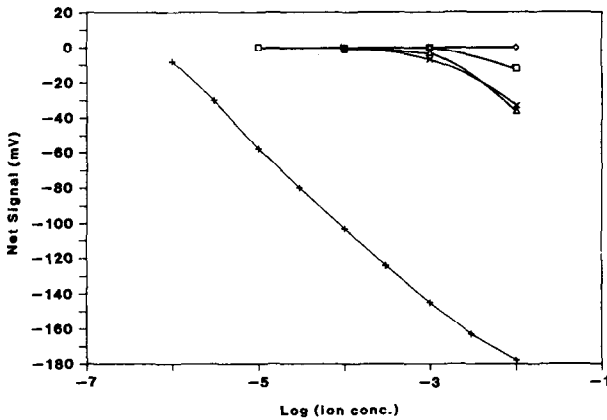

Fig. 6. Response of new SO_2 gas-sensing arrangement to various anions: (+) sulfite; (□) iodide; (◇) bromide; (×) thiocyanate; (△) thiosulfate.

as the recipient stream in the sulfur dioxide gas-sensing arrangement. However, the phosphate buffer, pH 10, used in the direct-probe work does not maintain a steady pH against a high influx of acidic gases from the sample stream. Given the high pH sensitivity of the polymer membrane, significant error can result from any drift of pH in the recipient stream pH. Thus, for sulfur dioxide sensing, 0.1 M MES buffer, pH 6, was chosen to make the system amenable to analysis of samples containing high acetate background, e.g., wine vinegar, which may contain ca. 100 mg l^{-1} sulfur dioxide in a background of 5% (v/v)

acetic acid. Experiments with this system have shown that measurements of mg l^{-1} levels of sulfur dioxide are easily made, even in samples containing 0.5% (v/v) acetic acid. This suggests that analyses of diluted wine vinegar samples (an analysis not possible with conventional Severinghaus-style sulfur dioxide sensors [30]) can be performed with this new sulfur dioxide gas-sensing arrangement. Concomitant with the pH stability achieved with the pH 6.0 buffer is the fact that response slopes toward sulfur dioxide are increased to nearly 50 mV/decade owing to the $Hg(DDC)_2$-based membrane response to a combination of sulfite and hydrogen sulfite.

Conclusions

The membrane electrode described in this report further demonstrates the concept of using organometallic complexes as membrane-active components in the design of new anion sensors. As shown here, such an approach can yield anion probes with selectivity patterns quite different than the classical Hofmeister sequence. While further studies are required to fully optimize the response characteristics and to elucidate the exact mechanism of the sulfite-sensitive electrode based on $Hg(DDC)_2$, it is likely that this new electrode will ultimately prove valuable for the selective measurement of sulfite species in a variety of samples, particularly when used in the more selective sulfur dioxide-sensing configuration.

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