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Solid Ion-Exchange Electrode Selective for Calcium Ion

Abstract. *A calcium-selective electrode with solid ion exchanger was prepared from a solution of the calcium salt of a dialkylphosphoric acid in collodion. The electrode responds rapidly and reproducibly to activity of calcium ion and demonstrates a selective response for calcium ion in the presence of alkaline earth and alkali metal cations.*

Measurement of calcium ion activity is of great practical importance in many areas of biology and geology. In an attempt to develop an electrode responsive to calcium and other divalent ions, a variety of materials have been investigated. Among the solid materials that have been shown to have a response to calcium ion are glasses (*1*), clays (*2*), ion-exchange resins supported in an inert matrix (*3*), and stearate multilayers (*4*). These substances, however, have little practical application because of poor selectivity or slow dynamic response, or both. A calcium-selective electrode that makes use of a liquid ion exchanger has recently been reported (*5*).

We report here a solid ion-exchanger electrode of simple construction which responds rapidly and selectively to calcium ion. This electrode has as its ion-sensitive element a solid solution of the calcium salt of a disubstituted organophosphoric acid in collodion. The characteristic behavior of this electrode is analogous to that of *p*H and cation-sensitive glass electrodes. The organophosphate salt provides exchangeable sites with a favorable selectivity for calcium ion while still allowing an appreciable calcium ion mobility within the solid phase.

The phosphoric acid employed should have carbon chains of sufficient length to render the compound essentially water-insoluble. Typically, dioctylphosphoric and didecylphosphoric acids are used. The calcium salt was prepared by neutralizing the acid with calcium carbonate and heating to 100°C to drive off the water and carbon dioxide that formed. The salt was then dissolved in three to five parts by weight of an alcohol-ether solution of collodion (*6*); a film or plug of the collodion solution was formed over the end of a 6-mm glass tube and dried for several hours at 50° to 60°C. After the exchanger had hardened, the tube was filled with 0.01*M* calcium chloride and fitted with a silver–silver chloride half-cell. Resistance of the electrode ranges from 1 to 10 megohms.

Potentiometric measurements were made with a Beckman research *p*H meter employing the cell

$$\mathrm{Ag}\;\Big|\;\mathrm{AgCl}\;\Big|\;\mathrm{CaCl_2}\;\Big|\;\begin{matrix}\text{Ion-exchange}\\ \text{membrane}\end{matrix}\;\Big|$$
$$\text{Test solution}\;\Big\|\;\mathrm{KCl\ (sat.)}\;\Big|\;\mathrm{Hg_2Cl_2}\;\Big|\;\mathrm{Hg} \qquad (1)$$

Individual ion activities were calculated from the extended Debye-Hückel equation, with the use of the correction given by Meites (*7*) at higher ionic strengths. Soaking the electrode in dilute calcium ion solution for several hours before initial use makes the response more stable and repeatable.

Figure 1 shows the response of the solid ion-exchanger electrode in solutions of calcium chloride, magnesium chloride, and calcium chloride plus 0.01*M* magnesium chloride. In solutions containing only a single salt, the observed potential (E) is given by a form of the Nernst equation

$$E = \text{constant} + \frac{2.303\ RT}{2F} \log a_{M^{2+}} \qquad (2)$$

where M is a divalent cation [in this case, calcium or magnesium (*1*)]; R, the gas constant; T, absolute temperature; F, the faraday; and a, activity. The constant includes terms relating to the choice of reference electrode, the reference electrode junction potential, and the calcium ion activity in the internal solution. The electrode behavior is Nernstian with respect to calcium ion over a concentration range of 10^{-1} to $10^{-4}M$ and to magnesium ion over a range of 10^{-1} to $10^{-3}M$. Plots of potential against the negative logarithm of metal ion activity are linear and yield a slope of 30 ± 1 mv per decade. Response to calcium and magnesium ion extends as low as 10^{-5} and $10^{-4}M$, respectively, but sensitivity in this range is diminished. At these levels the solubility of the calcium organophosphate possibly becomes a limiting factor.

Foreign cations moderate the electrode response to calcium ion by varying degrees. The upper curve in Fig. 1 describes the change in potential with calcium ion activity in the presence of 0.01*M* magnesium ion. From data of this type selectivity coefficients may be calculated which indicate the extent of the interference by other cations. The selectivity coefficient $K_{\mathrm{Ca}M}$ in Eq. 3,

$$E = \text{constant} + \frac{2.303\ RT}{2F} \times \log\left[\, a_{\mathrm{Ca}^{2+}} + K_{\mathrm{Ca}M}(a_{M^{z+}})^{2/z} \,\right] \qquad (3)$$

is defined in such a way that a value of $K_{\mathrm{Ca}M} < 1$ indicates a selectivity for $\mathrm{Ca^{2+}}$ relative to the ion M^{z+}, where z is charge. Table 1 lists values of $K_{\mathrm{Ca}M}$

Table 1. Selectivity coefficients of calcium dioctylphosphate–collodion electrode calculated from response in solutions of mixed ions.

Interfering ion	$K_{\mathrm{Ca}M}$
$\mathrm{Mg^{2+}}$	0.34
$\mathrm{Ba^{2+}}$	.90
$\mathrm{Na^{+}}$	.029
$\mathrm{K^{+}}$	.034
$\mathrm{H^{+}}$	1.5×10^4

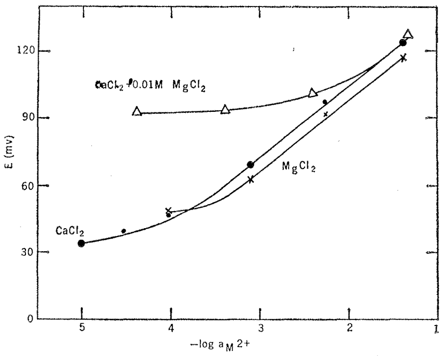

Fig. 1. Electrode potential at *p*H 8 plotted versus $-\log a_{\mathrm{Ca}^{2+}}$ for solutions of calcium chloride and calcium chloride in 0.01*M* magnesium chloride, and versus $-\log a_{\mathrm{Mg}^{2+}}$ for solutions of magnesium chloride. Electrode consists of 25 percent, by weight, calcium dioctylphosphate in collodion.

calculated for calcium ion relative to magnesium, barium, sodium, potassium, and hydrogen ions.

The data in Table 1 indicate that the dioctylphosphate-collodion electrode has a favorable response for calcium ion over magnesium, barium, sodium, and potassium ions. The calcium selectivity relative to the alkaline earth ions is at least as great as that of previous solid ion-exchange electrodes, and, in the case of the alkali metal ions, it is significantly greater. In addition, the calcium-hydrogen selectivity coefficient provides a wide range of useful *p*H for this electrode. In $10^{-2}M$ calcium chloride, the electrode potential is independent of hydrogen ion concentration from *p*H 3.5 to *p*H 10. A decrease in potential is observed above *p*H 10 and an increase below *p*H 3.5. The behavior at high *p*H is attributed to the formation of $CaOH^+$, to which the electrode is insensitive, inasmuch as the solubility product of calcium hydroxide is not exceeded at *p*H 10.

The dynamic response of the electrode is very rapid. In solutions containing no interfering cations, potential equilibrium following a step-functional change in calcium ion concentration is attained in a matter of 2 to 3 seconds. The speed of response is very much greater than that of previous solid ion-exchange electrodes which exhibited sensitivity for divalent metal ions.

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Lepidocrocite Iron Mineralization in Keratose Sponge Granules

Abstract. *Reddish-brown granules embedded in the spongin fibers of some keratose sponges consist of very fine crystallites of poorly organized lepidocrocite,* γ *FeOOH. This is the first occurrence of crystalline iron mineralization in the phylum Porifera and the first indication of hard tissue formation among the Keratosa.*

Crystalline iron compounds occur rarely as biologic precipitate except in the hydrous iron oxide making up the ferritin micelle. The most common and best documented of these occurrences are from the phylum Mollusca where radular teeth of certain chitons consist of magnetite (Fe_3O_4) (*1*) or magnetite plus lepidocrocite (γ FeOOH) (*2*). In addition the radular teeth of some groups of gastropods contain goethite (α FeOOH) (*3*). The sequence of iron mineralization in the magnetite radular teeth of *Cryptochiton stelleri* is the result of normal metabolic processes (*4*).

We report here on the occurrence of a crystalline iron mineral among Porifera and the first evidence of mineralization among the Keratosa (horny sponges). In certain species of keratose sponges the endosome is of a brick or rust-red color. This coloration varies in intensity from specimen to specimen and is caused by minute, strongly light-refracting particles attached to the fibers of the sponge skeleton (Fig. 1). The granules appear more or less spherical, are rusty brown, and vary in size between 0.5 and 2.5 μ (*5, 6*). These particles are intimately attached to and completely embedded in the spongin fibers.

Similar particles have been observed only in the genera *Spongia*, *Hippospongia* (which is very close to *Spongia*), and *Ircinia* (order Keratosa, family Spongiidae). Because the abundance of red coloration in *Spongia* (and therefore of the particles along the fibers) is correlated with other qualities, especially elasticity and durability (*7*), the commercially useful species and varieties have been most thoroughly studied. The so-called iron mold "Eisenfleck" (*6*) is usually more common and intense at the "root" of the sponge, the area of attachment to the substrate where the fiber network is particularly dense.

The nature of the particles as an iron-containing compound was first recognized by Herberger (*8*) who determined 8.7 to 8.9 percent iron oxide in the ash of the sponge skeleton. Other quantitative values of iron oxide from the literature vary between 1.55 percent (*9*) and 5 to 10 percent (*10*) of the ash. Values of 0.01 to 1.51 percent of the spongin dry weight were also measured (*6, 11*). By its positive Prussian blue reaction and a less successful ferricyanide test (Turnbull blue), Sella (*5*) found that ferric oxide is a major constitutent of the granules. Because of their irregular shape and distribution he concluded that they were not organic formations but foreign mineral grains. This has since become the accepted interpretation.

Living specimens of *Ircinia fasciculata* (Pallas) from an iron rail of *Concrete Ship*, a half-submerged wreck southeast of Bimini, Bahamas, were collected for study. Fibers and filaments of the animals showed strong development of granules. The specimens were immediately fixed in 96 percent ethanol and then transferred to 70 percent ethanol. Small pieces were fixed for electron microscopy in 6.25 percent glutaraldehyde at *p*H 7.2, postfixed in 4 percent osmium tetroxide at *p*H 7.4,

Table 1. Interplanar spacings (*d*) and relative intensities (*I*) of x-ray and electron-diffraction data from sponge granules compared with reference lepidocrocite (*13*). Abbreviations: VB, very broad; D, diffuse; S, strong; M, medium; W, weak.

Sponge granules				Lepidocrocite (x-ray)	
X-ray		Electron diffraction			
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6.85	VB, D			6.27	100
3.32	S	3.32	S	3.29	60
2.47	S	2.47	M	2.473	30
		2.39	W	2.362	15
				2.086	12
1.95	M	1.95	S	1.935	30
		1.86	VW	1.848	10
		1.74	VW	1.733	15
				1.567	8
1.53	M	1.53	S	1.532	7
				1.523	15
				1.493	2
				1.452	2
				1.436	7
				1.417	1
		1.39	W	1.391	3
				1.369	8
				1.264	1
		1.21	M	1.218	2
				1.201	2