determined by the nature of the interfaces present (15). Whether the presence of macromolecules or membranous components in cells brings about more specific or long-range alterations in either the orientation or the motion of the adjacent water molecules is a matter which will require much further study with many more welldefined model systems.

MARGARET C. NEVILLE

Department of Physiology, University of Colorado Medical Center, Denver 80220

CHRISTOPHER A. PATERSON Division of Ophthalmology, University of Colorado Medical Center

JAMES L. RAE Department of Ophthalmology, University of Texas Medical Branch,

Galveston 77550 DONALD E. WOESSNER

Mobil Research & Development Corp., Dallas, Texas 75221

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- 13. For two phases of water, ordered and normal, when exchange is sufficiently rapid,  $T (= T_1)$ or  $T_2$ ) is given by:

$$\frac{1}{T} = \frac{1-F}{T^{0}} + \frac{F}{T^{N}} = \frac{1}{T^{0}} + F\left(\frac{1}{T^{N}} - \frac{1}{T^{0}}\right)$$

where F is the fraction of normal water, and  $T^0$  and  $T^N$  refer to the ordered and normal phases, respectively. A plot of 1/T against F should be a straight line if the relaxation time of the ordered water does not change with water content. Such a plot of the data presented in Fig. 1 is not a straight line.

Under certain conditions, D can vary when the phase spacing is altered. However, the upper limit for D in lens cortex is the value 14 or pure water. Hence the maximum ratio of between cortex and nucleus is 3. The D between cortex and nucleus is 3. The ratio of  $T_2^*$  values is 5.2. This is consistent

with our conclusion that  $T_{a}^{*}$  and D are predominantly determined by different water fractions

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## **Carbonate Ion–Selective Membrane Electrode**

Abstract. A liquid membrane electrode has been developed with Nernstian response and a high selectivity for carbonate ion. The electrode responds rapidly to carbonate in the  $10^{-2}$ M to  $10^{-6}$ M range with a selectivity for carbonate over chloride, sulfate, and phosphate of at least 10<sup>3</sup> and negligible bicarbonate response. The electrode properties appear to be suited to chemical, biological, and oceanographic measurements.

Previous attempts (1, 2) to develop bicarbonate ion- or carbonate ionselective electrodes have resulted in electrodes with poor selectivity for the desired ion with respect to such common interferences as chloride. We have now succeeded in preparing a liquid membrane electrode with a selectivity for carbonate with respect to chloride, sulfate, and phosphate of at least 10<sup>3</sup> and negligible response to bicarbonate. The electrode exhibits Nernstian response to carbonate concentrations in the  $10^{-2}M$  to  $10^{-6}M$ range (Fig. 1) and has a response time, depending on the concentration



Fig. 1. Response of the electrode to varying carbonate activities. The solid line represents a Nernstian slope; E, electrode potential; a, activity.

levels employed of 30 seconds to 2 minutes.

The liquid membrane electrode has a conventional construction (2), with plastic electrode bodies (Orion) and cellulose acetate support membranes with an average pore diameter of 0.1 µm (Millipore Corporation) or Orion 92-20 membranes. The active electrode material is formed by means of a liquid phase consisting of 1 percent (by volume) of tricaprylyl methylammonium chloride (General Mills Chemicals, Inc., Aliquat 336) dissolved in trifluoroacetyl-p-butylbenzene. The latter is prepared by a Friedel-Crafts acetylation (3) of butylbenzene with trifluoroacetic anhydride with the use of anhydrous aluminum chloride catalyst, purified by fractional distillation, and identified by mass spectrometry [mass to charge ratio (m/e) =230], infrared spectroscopy, and nuclear magnetic resonance. The quaternary ammonium salt is used in the chloride form, as received, or may be converted to the bicarbonate form. An aqueous solution, 0.1M in both sodium chloride and sodium bicarbonate, is used as the internal electrode reference solution. All measurements are taken against a double-junction reference electrode (Orion).

Since carbonate coexists with bicarbonate in pH-dependent equilibrium, the carbonate concentrations for Fig. 1 are calculated from the relevant equilibrium constants (4) ( $K_1 = 4.5 \times$  $10^{-7}$ ,  $K_2 = 4.8 \times 10^{-11}$ ) and the modified Davies equation (5). The solid curve represents the theoretical Nernstian slope for a divalent anion, and the experimental points represent

1074

the results of three separate experiments that were conducted at varying pH values and total carbonate concentrations.

The data points indicate the absence of any response to the bicarbonate ion. Indeed, experiments carried out in mildly acidic mediums (pH < 5.5), where bicarbonate is vastly favored over carbonate, still yield potentials appropriate for a pure carbonate response even though the concentration of carbonate is less than  $10^{-8}M$ . In practical terms, however, the interconversion of carbonate with bicarbonate restricts the lower pH limit of the electrode to approximately pH 5.5. The electrode has an upper pH limit of approximately 8.5 at  $4 \times 10^{-3}M$ carbonate and 9.5 at  $5 \times 10^{-2}M$  carbonate.

Measurements carried out in mixtures of carbonate and chloride show negligible chloride interference even in samples containing  $10^{-1}M$  chloride and  $10^{-5}M$  carbonate. We calculate (6) the selectivity of carbonate to chloride of the electrode to be 5.4  $\times$  $10^3$ . This value should be regarded as a lower limit because of possible residual amounts of carbonate in the chloride reagent used. Similarly, we have determined the selectivity of carbonate to sulfate of the electrode as  $6.7 \times 10^3$  and that of carbonate to phosphate (taken as HPO<sub>4</sub><sup>2-</sup>) as 3.8  $\times$ 10<sup>3</sup>.

The overall potentiometric behavior of the new electrode is typical of liquid membrane electrodes in general. We observe response times ranging from 30 seconds to 2 minutes in carbonate solutions, the slowest response being found at the lowest concentrations. Electrical noise in carbonate solutions does not exceed 0.2 mv, and a reproducibility of  $\pm 0.5$  mv from sample to sample is readily achieved. The electrode lifetime in routine use will depend on such factors as the specific support membrane used and solution conditions, but it appears to be consistent with that reported for liquid membrane electrodes in general (2). In view of the dynamic range, selectivity, and other properties of this electrode, we expect it to be useful for carbonate measurements in biological, chemical, and oceanographic samples. H. B. HERMAN\*

# G. A. RECHNITZ

Department of Chemistry, State University of New York, Buffalo 14214

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### **Equatorial Jet in the Indian Ocean: Theory**

Abstract. A nonlinear numerical model and a simple analytical theory explain the basic features of the equatorial surface jet in the Indian Ocean recently reported by Wyrtki. The observed width of this transient current, 500 kilometers, is given theoretically by twice the baroclinic equatorial radius of deformation. The numerical model reproduces all Wyrtki's observations of this natural phenomenon.

During the transition periods between the two monsoon seasons, a narrow, high-speed surface jet flows along the equator from west to east across the entire Indian Ocean (1). We have been developing numerical models of the eastern boundary layer (2, 3) to study coastal upwelling. Wyrtki's report (1) encouraged us to use our model to explain the physics of this transient, wind-driven jet. In this report we derive theoretical estimates of the observed space and time scales given by Wyrtki.

In the numerical model the nonlinear, time-dependent primitive equations are solved for a two-layer, flatbottomed ocean on a beta plane (4). The independent variables are x (distance eastward), y (distance northward), and t (time). The dependent variables are the eastward and northward horizontal velocity components, u and v, respectively, and the thickness, h, of each layer. The equations are

These equations are well known, as are the details of their derivation (2). In this report we discuss a numerical solution of these equations and a simple analysis of a "stripped-down" linear version of this model.

Before presenting numerical results, we consider the simplest model of equatorial surface currents for the middle of the Indian Ocean, away from boundaries. If we let  $u = u_1 - u_2$ , v = $v_1 - v_2$ , and  $h = h_1$ , Yoshida (5) has shown that the equations

$$\frac{\partial u}{\partial t} = \beta yv + \tau_x^s / \rho H_1$$
$$\beta yu = -(g\Delta\rho/\rho) \frac{\partial h}{\partial y}$$
$$\left(\frac{1}{H_1} + \frac{1}{H_2}\right) \frac{\partial h}{\partial t} = -\frac{\partial v}{\partial y} \qquad (2)$$

may be used to deduce some understanding of the physics (6). In Eqs. 2,  $\beta$  is the coefficient of the latitude variation of f,  $\tau_x^{s}$  is the x component of  $\tau^{s}$ , and H is the initial value of h (capital letters denote initial values).

$$\begin{aligned} \frac{\partial \mathbf{v}_{1}}{\partial t} + \mathbf{v}_{1} \cdot \nabla \mathbf{v}_{1} + \mathbf{k} \times f\mathbf{v}_{1} &= -g\nabla(h_{1} + h_{2} + D) + (\tau^{s} - \tau^{T})/\rho h_{1} + A\nabla^{2}\mathbf{v}_{1} \\ \frac{\partial h_{1}}{\partial t} + \nabla \cdot h_{1}\mathbf{v}_{1} &= 0 \\ \frac{\partial \mathbf{v}_{2}}{\partial t} + \mathbf{v}_{2} \cdot \nabla \mathbf{v}_{2} + \mathbf{k} \times f\mathbf{v}_{2} &= -g\nabla(h_{1} + h_{2} + D) + g\frac{\Delta\rho}{\rho}\nabla h_{1} + (\tau^{T} - \tau^{B})/\rho h_{2} + A\nabla^{2}\mathbf{v}_{2} \\ \frac{\partial h_{2}}{\partial t} + \nabla \cdot h_{2}\mathbf{v}_{2} &= 0 \\ \mathbf{v}_{i} &= [u_{i}, v_{i}] \end{aligned}$$
(1)

where f is the Coriolis parameter; g is the acceleration of gravity; D is the height of the bottom topography above a reference level;  $\tau^{s}$ ,  $\tau^{I}$ , and  $\tau^{B}$  are the wind, interfacial, and bottom stresses;  $\rho$  is the density of the ocean;  $\Delta \rho$  is the density difference between the layers; and A is the horizontal eddy viscosity.

When  $\tau_x^{s}$  is a constant, impulsively applied, the north-south velocity, v, is a solution of the ordinary differential equation

$$L^4 \frac{\partial^2 v}{\partial y^2} - y^2 v = aLy \qquad (3)$$

1075