Reports and Letters

Neglected Aspects of Electroosmosis in Porous Bodies

Consideration of the process of electroosmosis reveals that conventional descriptions (*1*) of this phenomenon do not mention interesting and important features of electroosmotic flow in porous bodies.

Figure 1 shows a schematic representation of a plug of porous material (such as unglazed porcelain) that separates two compartments containing electrodes. Let us assume that these compartments contain a solution that is in equilibrium with the solution that fills the pores of the plug, and let us also assume that the electrode compartments are flushed with fresh solution at such a rate that, when voltage is applied to the electrodes, the products of electrolysis are swept out and the composition of the solution in the compartments remains practically unchanged.

At liquid-solid interfaces, such as are present inside the plug, segregation of electric charges commonly occurs, forming an electric double layer. When a gradient of electric potential is imposed on such a system, the segregation of charge results in electroosmosis in which the pore water moves, in relation to the plug, in the direction of the electrode that has the same polarity as the charge residing in the surface of the solid phase.

When the plug is immobile and its charge is equally immobile, conduction of electricity within the plug depends on (i) motion of the counter-ions toward the appropriate electrode, and (ii) motion, toward the opposite electrode, of the "co-ions" (that is, ions carrying charges of the same sign as the surface). In comparison with the solution in the electrode chambers, the conduction of electricity in the plug involves a greater transport of charge by counter-ions and a lesser transport by co-ions ("surface conduction"). This is consistent with the fact that the mobile charge present as counter-ions exceeds the mobile charge present as co-ions by the amount of immobile charge on the plug, whereas the mobile charges present as counter-ions and co-ions are equal in the electrode compartments.

According to Bloksma (*2*) the mobility of counter-ions in the plug is impaired by interaction with the plug charge; nevertheless, since the mobility of the plug charge itself is very small or zero, the transport number for the counter-ions in the pore water will always exceed the transport number for the same species in the electrode compartments. In addition, the electroosmotic flow (by forcing the co-ions to migrate upstream while the counter-ions move downstream) increases the transport number of the counter-ions.

It follows from the differences that exist in the mode of conduction of electricity in the pore water and in the electrode compartments that electrolytes will tend to accumulate at the outflow face of the plug and disappear at the inflow face.

This conclusion is readily apparent in Fig. 1. For this example it is assumed that all the counter-ions (black) are of a single species, all the co-ions (white) are also of a single species, and the two species have equal valence and equal mobilities in the electrode compartments. The lines *AA'*, *BB'*, and *CC'* designate the locations of imaginary planes that intersect the electrode compartments and the porous plug. Suppose that a potential difference is applied to the two electrodes and that, in unit time, 4 electrons are collected by the anode and 4 electrons are released by the cathode. In order to sustain this process at a constant rate, there must be a net transport on 4 valence electrons in unit time across each of the three planes designated. At the planes *AA'* and *CC'*, this requirement will be met by the movement of 2 counter-ions and 2 co-ions that cross the planes in opposite directions. It has already been shown that, in the plug, the conduction of electricity involves a greater movement of counter-ions than of co-ions. This is represented in Fig. 1 by 3 monovalent counter-ions crossing the plane *BB'* in unit time, while only 1 monovalent co-ion crosses in the opposite direction, maintaining the requirement of a net transport of 4 valence electrons.

Since the events at the three planes designated are representative of events at all similar planes in the three parts of the system, discontinuities must occur at the inflow and outflow faces of the plug. It can be seen by inspection that, at the outflow face, one more counter-ion and one more co-ion will arrive in unit time than will depart, and salt will accumulate at that face. Inspection also reveals that salt will simultaneously be depleted at the inflow face. Thus, a concentration peak will develop at the outflow face and a concentration trough at the inflow face.

This accumulation-depletion process has an interesting consequence with respect to the stresses in the pore water during electroosmosis. Since the accumulation of electrolyte at the outflow face depresses the zeta potential and, by increasing the conductivity, lowers the gradient of the applied potential, the tendency for electroosmotic flow diminishes in the vicinity of the outflow face. The opposite is true at the inflow face.

If the plug is saturated with water, the total water flux must be constant along the length of the plug, in spite of differences in the tendency for electroosmotic flow. As a result, stresses must appear in the pore water in the plug. Under the circumstances of this example, the pressure in the pore water will everywhere exceed the pressure at the same level in the electrode compartments and the gradient of pressure must be directed outwards at each face. One would anticipate that a pressure maximum would occur in the plug in the vicinity of the inflow face for the following reasons: (i) The zone of electrolyte accumulation is constantly being displaced outward at the discharge face by the migration of the pore water, while the zone of depletion tends to spread into the plug from the inflow face for the same reason. (ii) An increment of electrolyte depletion will have a larger effect on the conductivity (and, hence, on the gradient of the applied potential) than a similar increment of accumulation. Both of these effects do more to favor electroosmotic flow at the inflow face than to discourage it at the outflow face. This in turn causes

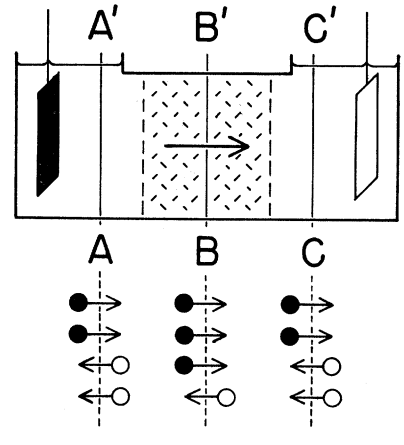

Fig. 1. (Top) Porous plug separating two electrode compartments. Electroosmotic flow is from left to right. (Bottom) Conduction of electricity by counter-ions (black) and co-ions (white) across planes *AA'*, *BB'*, and *CC'*.

a pressure maximum to occur within the zone in which depletion has occurred.

Between the inflow face and the pressure maximum a hydraulic countercurrent moves toward the inflow face along the central portion of the pores, while the electroosmotic flow occurs at the periphery. Between the outflow face and the pressure maximum, hydraulic flow and electroosmotic flow are in the same direction. In both cases the net flow is the same.

If the plug lacks homogeneity or if the solution in the electrode compartments is not one that would be in equilibrium with the original pore water, or if other conditions are altered, a variety of stress conditions may be induced in the pore water, including pore-water tensions (*3*). The point to be made at this time is that, even when the electrode compartments are flushed with a solution that is nominally in equilibrium with the pore water, initiation of electroosmotic flow induces processes that destroy the initial homogeneity of the pore water, distorting the applied electric field, altering the zeta potential, and confounding hydraulic and electroosmotic flow. The system is simply defined only at zero time, and measurements should be interpreted on this basis.

Zeta potentials computed by conventional methods from measurements of electroosmosis may be in error if it is assumed that the composition and pressure of the pore water remains unaffected by the process.

A more detailed analysis of electroosmotic flow in clay soils, together with pertinent experimental data, is in preparation (*4*).

R. D. MILLER

Department of Agronomy,
Cornell University, Ithaca, New York

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4. This work is being conducted at Harvard University under Department of the Navy contract NOy-76303.

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Serotonin Release as a Possible Mechanism of Reserpine Action

Previous communications have reported certain similarities in the physiologic actions of reserpine, a tranquillizing agent, and serotonin (5-hydroxytryptamine), a substance postulated to have a role in brain function (*1*). Both compounds show sedative effects in mice and potentiate the action of certain hypnotics by a central mechanism (*2*). The potentiation caused by either substance is antagonized by pretreatment with lysergic acid diethylamide (*3*), a compound that blocks the effects of serotonin on smooth muscles (*4*) and produces psychotic states in man (*5*).

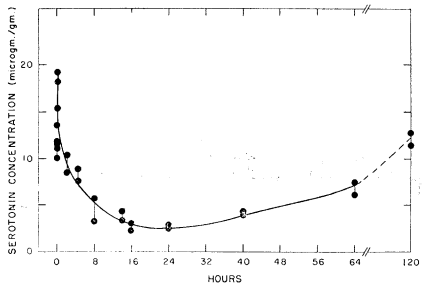

Fig. 1. Serotonin concentration in small intestine at various times after administration of reserpine. The points at zero time denote serotonin concentration in controls. The other points denote the serotonin concentration after administration of reserpine (5 mg/kg) to rabbits intraperitoneally (100 mg of reserpine was dissolved in a few drops of glacial acetic acid and diluted with 4 ml of propylene glycol, 4 ml of ethanol, and 8 ml of water).

It was also demonstrated that administration of relatively large doses of reserpine to dogs markedly increases the urinary excretion of 5-hydroxy-indoleacetic acid (*3*), a major metabolite of serotonin (*6*). These observations suggested that certain actions of reserpine are mediated through liberation of serotonin (*3*). The present communication describes experiments that show by direct analysis that reserpine effects the release of serotonin from the intestine, a major depot of serotonin in the body.

Rabbits received 5 mg/kg of reserpine intraperitoneally. Untreated rabbits served as controls. At various times after drug administration, animals were killed and 10 g of small intestine adjoining the stomach was removed, cut open, and washed with isotonic saline. The tissue was homogenized in 2 vol of 0.2*N* HCl, and the serotonin in the homogenate was measured by modification of the method of Udenfriend *et al.* (*7*). This method involves extraction of the serotonin into butanol, reextraction into dilute acid, and the formation of a colored derivative by reaction with α-nitroso-β-naphthol and nitrous acid. Application of the method to intestinal tissue disclosed the presence of a small amount of interfering material that also reacted with the nitrosonaphthol reagent. The interfering color was removed by shaking the solution of colored products with butanol.

Serotonin content of the small intestine declined progressively for about 16 hr after reserpine administration, finally reaching a concentration 15 to 20 percent of that of the average normal value (Fig. 1). The concentration of serotonin remained at this low level for about 16 hr and then increased slowly, reaching the normal value after about 5 days.

The apparent serotonin in the tissue appeared to be identical with authentic serotonin as shown by comparison of fluorescence spectra (3*N* HCl) using a spectrophotofluorometer previously described (*8*), and by comparison of the absorption spectra of the nitrosonaphthol reaction products. In addition, on chromatographing the intestinal extract on paper (*n*-butanol-1*N* ammonia), the major amount of material fluorescing in acid and forming a blue color with *p*-dimethylaminobenzaldehyde showed the same R_f value as serotonin.

The effect of various doses of reserpine on the content of serotonin in small intestine was determined. As the dose was reduced, the decline in serotonin became gradually smaller but seemed evident with as little as 0.25 mg/kg of reserpine (Fig. 2).

The serotonin content of the whole intestinal tract was determined following the administration of reserpine. In three untreated rabbits, weighing about 2 kg each, the intestines contained an average of approximately 1000 μg of serotonin. Sixteen hours after the administration of 5 mg/kg of reserpine, the content of serotonin in the intestines of three animals averaged 350 μg. Thus the reserpine had caused the liberation of about 650 μg of serotonin from this tissue.

A number of rabbits, especially those given the larger doses of reserpine, had diarrhea. Consequently, the effect of laxatives in purgative dosage (castor oil and magnesium sulfate) and of a cholinergic agent (prostigmine 0.3 mg/kg in three divided doses) was determined. These substances did not change the serotonin content of the intestine. Sedation per se did not effect serotonin release, since heavy barbital and phenobarbital narcosis for 12 hr failed to lower the serotonin content of the intestines.

Experiments described in this paper

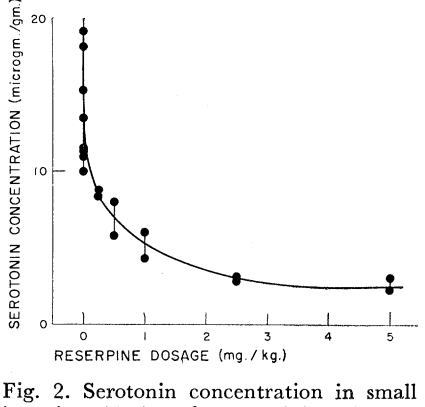

Fig. 2. Serotonin concentration in small intestine 16 hr after administration of various doses of reserpine.