Inorganic Membrane Electrodes[1]

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Several types of membranes have been studied and used as indicating electrodes. Foremost is the glass electrode for pH measurement. Other types include collodion membranes (2,5), membranes of clay minerals and ion exchange membranes (3,4). In addition, inorganic ionic precipitates have been formed into membranes. An earlier report from this laboratory (1) described the preparation of such membranes using a paraffin binder and their application as potentiometric indicating electrodes. The potentiometric data were interpreted on the basis that the surfaces of the inorganic particles assume an electrical charge, determined jointly by the precipitate and the composition of the electrolyte solution in contact with it, thereby permitting oppositely charged counter ions to pass through the membrane. This type of membrane can be useful as an indicating electrode, although irreproducibility and incomplete selectivity are serious limitations, and also as a means of measuring the surface electrical properties of the material of which the membrane is composed.

The purpose of the present report is to describe results of experiments on the "electrical rectifier" properties of the membranes and on radiotracer experiments designed to ascertain more specifically the ion transport characteristics of the membranes.

Membranes As Rectifiers

The membranes should function as electrical rectifiers if they preferentially permit either cations or anions to pass, as prior data show (1). This phenomenon was investigated by a d-c conductance method. Deionized water was placed on one side of the membrane, which was sealed across the end of a glass tube, and an electrolyte solution on the other side. The passage of electrical current through the membrane must consist of the flow of ions through the membrane, and this ion flow must be predominately from the electrolyte side to the water side because the water side has relatively very few ions available for flow. The electrical conductance was measured first with the water side positive, so anions must pass through the membrane, and then with the same side negative, so cations must pass through. The ratio of the d-c conductances in the two directions of applied potential is a measure of the rectifier property of the membrane and thereby a measure of the membrane's preference to pass cations or anions.

It was found that a time factor was significant. The observed membrane conductance changed as the potential was continuously applied in either direction. Constant readings were not obtained in fifteen minutes and longer in some cases, with the current flow during measurement ranging from a few microamperes to several milliamperes. It was also found that, the longer the potential was left on in one direction, the longer

it took to approach an approximately constant conductance in the opposite direction. Repeated short cycling of the applied potential did not improve the situation significantly. Therefore the magnitudes of the conductances and conductance ratios are not quantitatively meaningful, but the identification as to whether cations or anions are preferentially passed through the membrane is very definite.

Data of typical measurements on membranes of several compositions are listed in table 1.

TABLE 1. Rectifier Data on Membranes

Membrane	Test Electrolyte	Preference	Conductance Ratio for cations for anions
$BaSO_4$ in paraffin	$BaCl_2$	anion	0.26
	Na_2SO_4	cation	1.40
Apatite[1] in paraffin	$CaCl_2$	anion	0.50
	Na_3PO_4	cation	1.35
	KCl	anion	0.88
Apatite[2]	$CaCl_2$	anion	0.57
	Na_3PO_4	cation	1.72
	KCl	anion	0.85
$Ni(H_2C_4H_6N_2O_2)_2$ in paraffin	$NiCl_2$	anion	0.87
	$H_2C_4H_6N_2O_2$	cation	1.4
$Fe_2O_3 \cdot xH_2O$ (air-dried) in paraffin	NH_4OH	cation	1.25
	$FeCl_3$	anion	0.63
Fe_2O_3 in paraffin	NH_4OH	cation	1.5
	$FeCl_3$	anion	0.8

1. Powdered dental enamel, chiefly calcium hydroxy phosphate.
2. A slab of dental enamel from a human tooth.

The preferences are the same as those found in the potentiometric measurements (1) except for those of $FeCl_3$ solutions with both types of Fe_2O_3 membranes. The general agreement substantiates the concept that each precipitate preferentially adsorbs as a primary layer whichever lattice ion is available in the test electrolyte and permits preferential passage of the oppositely charged counter ions.

The rectifier-type measurements are of interest for straight-forward analytical applications, because in a precipitation titration the medium should change from one causing cation preference to one causing anion preference, or vice versa, upon passing through the region of the equivalence point. The time factor, however, makes the method impractical for titrations, although these measurements are useful in providing information on the surface electrical properties of precipitates.

Radiotracer Experiments on the Membranes

Radiotracer experiments were undertaken to obtain direct verification of the concept of ion transport through membranes of barium sulfate in

paraffin. Several series of experiments were run, using active Ba-133 as $BaCl_2$ and active Cl-36 as NaCl. In each experiment the active solution was placed on one side of the membrane and deionized water was placed on the other side. Aliquots of the latter were subsequently withdrawn for counting.

In the first series of experiments, using $Ba^{133}Cl_2$ and making potential measurements simultaneously, it was found that essentially no active Ba^{++} was transported through the membrane, even after potential equilibrium was established. Upon subsequent soaking of both sides of each membrane in water, much more active Ba^{++} was desorbed from the side initially in contact with the active solution than from the other side. Therefore, it is concluded that $BaSO_4$ membranes in contact with $BaCl_2$ solution, pass very little or no barium ions, a conclusion in full agreement with the rectifier and potentiometric conclusions that anions are preferentially passed.

Several series of experiments with deionized water on one side of the membrane and a solution of $NaCl^{36}$ plus either $BaCl_2$ or Na_2SO_4 on the other side, revealed a somewhat greater passage of Cl^- when under the influence of Na_2SO_4 than when under the influence of $BaCl_2$. This observation appears at first to contradict the potentiometric and rectifier data, which indicated a cation preference with Na_2SO_4 and an anion preference with $BaCl_2$. It is felt, however, that all three types of observation can be combined into a single concept, as follows.

None of the potentiometric or rectifier-type data reveal a complete preference for either cation or anion transport. Thus the "pores" through the membrane, which certainly must exist for any ion passage to occur, must be sufficiently large so that the electrical charges upon the surfaces of the particles within the membrane do not exert influence throughout the entire cross-section of the pore. As a group of ions enters a pore, that ion which forms the tightly-held primary adsorption layer is held back most tightly, that ion which forms the less tightly-held counter ion layer is held back slightly, and other ions are retarded only by such factors as ion mobility and are not influenced by the walls of the pore at all. Thus, with a $BaSO_4$ membrane and an electrolyte of Ba^{++} Cl^- and Na^+ ions, the Ba^{++} ion is held back most tightly, oppositely charged Cl^- ion is held back somewhat, and Na^+ ion is not held back at all by the $BaSO_4$ surfaces along the pores. Alternatively, with an electrolyte consisting of Na^+, $SO_4^=$ and Cl^- ions, the $SO_4^=$ ion is held back most tightly, the oppositely charged Na^+ ion somewhat, and the Cl^- ion not at all. This concept of the mechanism is consistent with the radiotracer data, in that Ba^{++} results in Cl^{36} ions being held back somewhat while $SO_4^=$ results in no specific retardation of Cl^{36} ions. The concept is also consistent with the potentiometric and rectifier-type data, in that Ba^{++} causes a preference for anion passage (the ion held back most tightly is a cation) while $SO_4^=$ causes a preference for cation passage (the ion held back most tightly is an anion).

If this concept is correct, a membrane should retain Cl^{36} more tenaciously after treatment with Ba^{++} solution than after treatment with $SO_4^=$ solution, even though the latter passes more Cl^{36} than the former. Such was invariably found to be the case. Therefore it is now felt that this visualization of the mechanism whereby ions pass through the membranes provides a valid means of correlating the three types of measurement—

potentiometric, rectifier-type and radiotracer. It is further felt that the concept is fully consistent with zeta potential measurements upon similar materials and with generally accepted concepts of adsorption of ions upon the surfaces of ionic precipitates.

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