TECHNICAL PAPERS

Some Electrochemical Properties of Shales

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The application of glass membranes to the comparison of hydrogen ion activities in aqueous solutions suggests similar applications of other membranes for the purpose of determining the activities of other cations. In this connection recent work by Marshall and others (*2–4*) has been very significant. Initially, Marshall examined the applicability of some natural zeolites to activity determinations, but, finding these unsatisfactory, achieved greater success with membranes (0.1–0.5 mm thick) prepared from a number of hydrogen clays. In general, Marshall found that these clay membranes gave rise to potentials which, for concentrations below 0.1 molal of such monovalent cations as K^+ and Na^+, obeyed the Nernst equation.

At concentrations in excess of about 0.1 molal the potentials across the clay membranes were found by Marshall to be always less than those anticipated from the Nernst equation. He applied to his results the equation developed separately by Meyer and Sievers (*5*) and Teorell (*6*) for the potential across a membrane separating two solutions of the symmetrical valence type, viz.,

$$E=\frac{RT}{F}\left[U\ln\frac{\left(\frac{4a_2^2}{A^2}+1\right)^{\frac{1}{2}}+U}{\left(\frac{4a_1^2}{A^2}+1\right)^{\frac{1}{2}}+U}+\frac{\ln}{2}\,\frac{\left\{\left(\frac{4a_1^2}{A^2}+1\right)^{\frac{1}{2}}+1\right\}\left\{\left(\frac{4a_2^2}{A^2}+1\right)^{\frac{1}{2}}-1\right\}}{\left\{\left(\frac{4a_1^2}{A^2}+1\right)^{\frac{1}{2}}-1\right\}\left\{\left(\frac{4a_2^2}{A^2}+1\right)^{\frac{1}{2}}+1\right\}}\right],$$

where $U=\frac{U_c-U_A}{U_c+U_A}$, U_c, U_A are the mobilities of the cation and anion within the membrane, $A=$ the charge on the membrane expressed as an ionic activity, and a_1 and a_2 are the molal activities of the solutions on each side of the membrane.

Marshall inferred that one possible effect of concentrated salt solutions on the membranes he had prepared was a reduction in the effective value of A, the charge upon the membrane.

The calculation of theoretical potentials across a membrane depends upon the determination of single ion activities. Single ion activities are not calculable thermodynamically, but by making certain nonthermodynamic assumptions it is probable that they can be estimated with reasonable accuracy for dilute salt solutions. These assumptions are: (a) that in dilute potassium chloride solutions the activity of K^+ is equal to Cl^-, and (b) that for dilute solutions of other chlorides the activity of the chloride ion is the same as that of the chloride ion in a solution of potassium chloride of the same ionic strength. The precise accuracy of these assumptions is unknown, but their inaccuracy does not appear to be a fundamental reason for the lack of agreement between measured and calculated potentials noted by Marshall when considering monovalent cations of concentration greater than 0.1 molal. In Table 1 the writer has used these same assumptions to compute sodium ion activities in sodium chloride solutions up to approximately 1.0 molal. The activity coefficients of sodium and potassium chloride given by Latimer (*1*) were used. No attempt has been made to compute single ion activities for sodium chloride solutions of concentrations in excess of 1.0 molal.

For the determinations reported here certain natural shales have been employed as membranes—possibly barriers would be a preferable term considering the thicknesses involved. Sodium chloride solutions are so far the only ones examined in any detail. These shales consisted of two distinct types, both obtained by rotary drilling using a diamond bit. The first type used was Conemaugh shale of Pennsylvanian age taken from depths relative to ground level ranging from 26′ to 89′. The upper portions of this shale are red; the lower, dark gray. The second type was Woodford carbonaceous shale of Devonian age from a depth, relative to ground level, of 6,808′. All specimens of both types were air-dried for about a year.

Specimens selected for test were carefully examined for cracks parallel to the bedding planes of the shale; those obviously cracked were rejected. The specimens were then mounted in a number of different ways, all of which proved satisfactory. Broadly speaking, however, the methods fell into two distinct categories. In each case the sodium chloride solutions were in contact with a cleavage surface of the shale, *i.e.* current flow from solution to solution was normal to the bedding planes. In the first method this was achieved by wax-cementing[1] a flanged male 24/40 standard taper to each face of the cylindrical shale specimen. L-shaped tubes with an i. d. of 2.5 cm and with vertical limb 15 cm high and horizontal 9 cm long, including the 24/40 female taper, were then attached to hold the sodium chloride solutions. In this method it has been found that length of shale is immaterial if the specimen is not cracked. About 3 cm is a convenient length. In the second method small chips of shale are cemented by their cleavage surfaces to the ends of glass tubes 20 mm in diameter. The sides of the shale chips are then coated with wax and also the exterior face with the exception of a hole about 5 mm in diameter. One saline solution is put into the 20-mm tube and an-

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[1] The green optical pitch was No. 17, supplied by Musto, Keenan and Company, 1801 South Soto Street, Los Angeles 23, California. A suitable wax for cementing the glass to shale can be made of 100 gm of green optical pitch to which 1 cc of lubricating oil has been added.

other into a beaker in which the tube is immersed. The resistance of shale specimens so mounted varies, but the total resistance is of the order of 10,000–20,000 ohms, and satisfactory potential readings can be made with a Leeds & Northrup Type K potentiometer. A thermionic amplifier is not necessary unless the total resistance exceeds 20,000 ohms. Saturated calomel electrodes were employed as measuring electrodes, the usual precautions being taken to ensure reproducible boundary potentials between the saline solutions and the saturated potassium chloride bridges.

Results obtained using the shales to separate sodium chloride solutions of various molalities were very consistent provided the shales used were uncracked. Where appreciable cracking was present but unnoticed prior to mounting the specimens, erratic potentials were immediately observed, and the cracks themselves soon became visible, the shales frequently shearing at the point of cracking. Attainment of equilibrium after changing the saline solutions was usually rapid unless a big change in the concentration of the solutions had been made, in which case equilibrium was only achieved after a period of days with frequent changing of the sodium chloride solutions.

TABLE 1

Shale type	a_1	a_2	Calculated potential (mv)	Observed potential (mv)
Conemaugh Woodford	0.0398	0.0101	32.7	32.7
Conemaugh Woodford	0.395	0.0995	32.2	32.2
Conemaugh Woodford	0.719	0.2856	23.3	23.0

TABLE 2

Shale type	C_1 molal	C_2 molal	Potential from conductivity	Observed potential (mv)
Conemaugh	2.0	0.5	30.1	14.3
"	4.0	1.0	23.7	9.9
Woodford	2.0	0.5	30.1	34.2
"	4.0	1.0	23.7	28.9
"	Saturated	0.01	133.5	137.2

In Tables 1 and 2, calculated potentials up to 1.0 molal have been derived from activities in the manner discussed above. For concentrations between 1.0 molal and saturation each ratio of the sodium ion activities in the Nernst equation has been replaced by the comparable ratio of the conductivities of the two sodium chloride solutions. This has been done because the computation of sodium ion activities at very high concentrations involves large uncertainties. The conductivity data used are not of the highest accuracy, but comparison of potentials calculated from the conductivities with observed values serve to show that the analogous shale potentials recorded in the electrical well logging of deep boreholes may be used to obtain an estimate of the conductivity of the saline fluids in petroleum reservoir rocks (*7*). Results are for a temperature of 20° C.

The data show that both the Conemaugh and Woodford shales appear to have marked sodium electrode properties at concentrations up to 1.0 molal, but beyond this concentration the ability of the Conemaugh to give potentials of the magnitude required by the Nernst equation is markedly inferior to that of the Woodford. This difference in behavior probably results from the varying nature of the minerals and interstitial waters in the two shales. In the case of Conemaugh shales there were no electrochemical differences between the red and gray facies examined, indicating that the state of reduction of the iron in the shales is not a primary factor.

No theory to cover the behavior of the Woodford shale is at present available, but the results show that it may be possible to produce a membrane from shales which will encompass an activity range, for sodium ions, considerably wider than that covered by any of Marshall's prepared clay electrodes. Assuming that it is justifiable to extend the application of the Meyer and Sievers and Teorell theories to cover the very high sodium chloride concentrations used in these experiments, it would appear that the thermodynamic charge, A, on the shale minerals —possibly the clay minerals in the shales—is relatively very large. Work on shale membranes is continuing.

References

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Carbon Dioxide, Cerebellum, Chloramines, and Convulsions

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During the past two years much light has been shed on the problem of the convulsant agent in bleached flour. Since the observation of Mellanby in December 1946 (*4*), that treatment of flour with nitrogen trichloride as used commercially makes such flour toxic to dogs, there has been much speculation regarding the possible effect of such a diet on man. Human experimentation is being carried on in at least three institutions, and it is too early to evaluate results obtained thus far.