[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

Electrokinetics. XV. The Use of Inert Electrodes in Measuring the Streaming Potential[1]

BY HENRY B. BULL

D. R. Briggs[2] developed a method for measuring the streaming potential of a diaphragm of cellulose fibers packed between two inert perforated gold electrodes. Briggs thus dispensed with the use of the clumsy calomel half-cells usually employed in measurements of the streaming potential. Contamination by electrolytes from the half cells was thus avoided. This is an important point. It is the author's belief that many of the divergent data encountered in streaming potential work can be traced back to this difficulty. There has been, however, some feeling that the use of inert electrodes in this connection is not a legitimate one.

Bull and Gortner[3] entered into a preliminary discussion of these things. They believed that inert electrodes could be used with a quadrant electrometer as proposed by Briggs because (1) the data obtained are reproducible and (2) a straight line is obtained when the pressure forcing the liquid through the diaphragm is plotted against the observed streaming potential. Such would not have been the case if the gold electrodes had not responded in a reversible way. It seemed best, however, to subject the use of gold electrodes to a more rigorous test. This has been done.

Experimental

The measuring device was that employed by Bull and Gortner[3] and consists of a Dolezalek quadrant electrometer used as a null instrument, the streaming potential being balanced against the potential from a Leeds and Northrup type K potentiometer. A Pyrex glass capillary was substituted for the cellulose diaphragm. This arrangement has been described by Bull.[4] The Pyrex capillary was 20 cm. long and 1 mm. in diameter. The capillary had ground glass ends which fitted into ground glass cups. No rubber connections came in contact with the solutions. An aqueous solution of 1×10^{-4} sodium chloride was used. The inert electrodes were bright platinum wires which were fused into the glass tubes leading to the capillary and were about 3 cm. from each end of the capillary. Very small glass capillaries were attached close to the platinum electrodes. They were filled with agar and saturated potassium chloride and dipped into saturated calomel half cells. The sodium chloride solution was streamed through the long capillary until equilibrium had been reached. Streaming potential measurements were then made first with the platinum electrodes and then with the calomel half cells. The results are shown in Fig. 1.

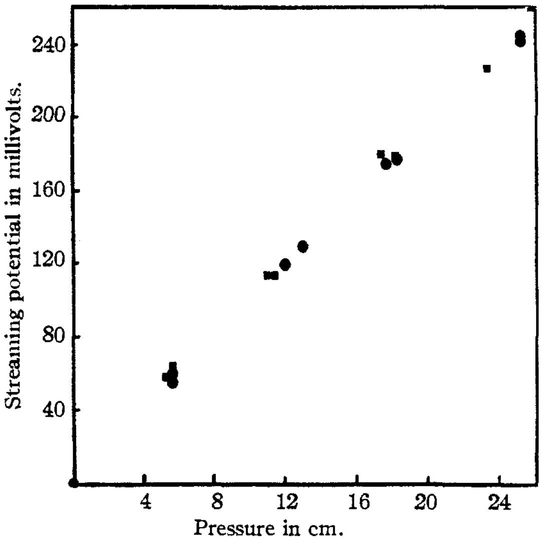

Fig. 1.—●, HgCl–Hg electrodes; ■, Pt electrodes.

Discussion

As can be seen, the values obtained with the inert platinum electrodes agree completely with those obtained with the calomel half cells. This is in keeping with the results of P. A. Van der Meulen and F. Wilcoxon,[5] who were able to use bright platinum as a reversible electrode in titrations.

On the basis of the experiments reported in this paper, and on numerous other experiments in the preceding papers in this series as well as on extentive unpublished data, it seems highly desirable that in all future work on streaming potential,

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(2) D. R. Briggs, *J. Phys. Chem.*, **32**, 641–675 (1928).

(3) Bull and Gortner, *ibid.*, **35**, 310–330 (1931).

(4) Bull, *Kolloid-Z.*, **66**, 20 (1934).

(5) P. A. Van der Meulen and F. Wilcoxon, *Ind. Eng. Chem.*, **15**, 62 (1923).

platinum or gold electrodes be substituted for the usual calomel half cells to avoid a dangerous source of contamination.

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Reactions of Thionyl Chloride and of its Thermal Decomposition Products with Oxalates and Formates

BY WALTER C. SCHUMB AND CLEMENT H. HAMBLET

In the course of a study of the thermal decomposition of thionyl chloride, it was found necessary to determine the quantity of undecomposed thionyl chloride in the presence of its decomposition products, *viz.*, sulfur monochloride and dichloride, chlorine and sulfur dioxide.[1] Among the various reactants which were considered for this purpose, lead oxalate and lead formate were found to offer the most promise. Both react readily with thionyl chloride with the production of carbon monoxide, but since the exact nature of the reactions involved does not appear to have been established, it was considered of interest to investigate these reactions quantitatively, and to study also the reactions of the decomposition products of thionyl chloride with the same lead salts. As a result of this investigation, the nature of these reactions has been established, and, in addition, a method has been devised by which unchanged thionyl chloride may be determined in the presence of its decomposition products.

Preparation and Purification of Materials

Nitrogen.—Purified nitrogen was used in all of these experiments to sweep out the system and to carry along the vapors of volatile substances formed therein. Commercial nitrogen was purified by passage in succession through concentrated sulfuric acid, sodium hydroxide on asbestos ("Ascarite") and a tube 91 cm. long containing metallic copper (wire form, reduced from the oxide) at 550°. To eliminate hydrogen, which appeared to be evolved slowly by the reduced copper, the gas was passed over copper oxide at 550°, and the final drying of the gas was by means of anhydrous barium perchlorate ("Desicchlora") and phosphorus pentoxide (resublimed in oxygen).

Thionyl Chloride.—The thionyl chloride was obtained by purifying Eastman thionyl chloride (b. p. 76–78°) according to the method of Meyer and Turnau[2] in an all-glass apparatus, and was preserved in small, sealed capsules until ready for use.

As a criterion of the purity of this product, the heating curve of a portion was determined by means of an apparatus similar to that employed by Skau.[3] Since the flat portion of the curve, during which the temperature remained constant within five microvolts, lasted half the period during which actual melting was taking place, the thionyl chloride was considered to be of a high degree of purity. The melting point of thionyl chloride, as taken from the flattest part of this curve, was $-101.4°$, a value somewhat higher than the value ($-104.5°$) reported by Mayes and Partington.[4]

Sulfur Monochloride.—Sulfur monochloride (Merck) was purified by the method recommended by Pope, *et al.*[5] The all-glass apparatus was constructed so that the fractional distillations could be carried out, and the purified samples sealed off in small capsules, all in the absence of air.

"Sulfur Dichloride" Mixture.—Since sulfur dichloride is unstable at ordinary temperature, the pure substance could not be used; consequently a mixture of sulfur monochloride saturated at 0° with chlorine gas was employed. Commercial chlorine was dried by concentrated sulfuric acid, and then bubbled through 100 cc. of purified sulfur monochloride at 0°, at the rate of 1 cc. per second for forty-eight hours. At the end of this time, since the mixture showed no further deepening of color, the product was thoroughly frozen, and, after the system had been evacuated, distilled with the aid of liquid air into capsules, and sealed off.

Chlorine and Sulfur Dioxide.—These gases were dried by passage through concentrated sulfuric acid.

Lead Oxalate.—The lead oxalate used in the study of the individual reactions was a commercial product of good quality, and was not further purified. In the determination of the precision of the method of analysis for thionyl chloride in the presence of its decomposition products, the lead oxalate used was prepared metathetically from a slight excess of reagent quality oxalic acid and lead acetate. The product was washed with cold water and alcohol, and dried at 140°. Upon titration with potassium permanganate, the material was found to be 100.0% PbC_2O_4 on the basis of its reducing power.

Lead Formate.—The lead formate used was prepared by the action of a slight excess of formic acid on lead carbonate. The product was crystallized at 0°, washed with water, and dried at 110°. Titration of the crystals by the method of Blackadder[6] showed that on the basis of its

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[1] Heumann and Kochlin, *Ber.*, **16**, 1628 (1883).

[2] Meyer and Turnau, *Monatsh.*, **28**, 153 (1907).

[3] Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

[4] Mayes and Partington, *J. Chem. Soc.*, 2594 (1926).

[5] Pope, *et al.*, *ibid.*, **119**, 634 (1921).

[6] Treadwell–Hall, "Analytical Chemistry," 1930, p. 532.