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ABSTRACT

A cell has been designed and built that allows for rapid measurement of volume moved in a definite time by electroosmosis. The cell is simple to use and is not very elaborate. Using a water jacket, the cell temperature can be controlled to ± 0.1° C. Measurements are presented for acetonitrile, dimethylformamide, and nitrobenzene at 25° C for applied voltages of 25, 50, 75, and 100 volts.

I. INTRODUCTION

Interest in electroosmotic measurements and especially a cell for rapid measurements arose from attempts to use this phenomenon in electrical circuits. It was believed that electroosmosis could be used for the opening and closing of a switch in an electrochemical relay.

Electroosmosis is a definite phenomena of a system and therefore would have a high reliability. Since each liquid, colloid, or mixture of liquids have different electroosmotic properties, a variety of times would be available for a relay by just changing the chemical component. The operating temperature would cause some limitations on the choice of systems, but many organic liquids could be used over the standard operating range (-65 to +165° F). However, electroosmosis has a temperature dependence and this would have to be studied for most systems to see what its magnitude is.

Since it would be desirable to look at many systems that have not ben studied in great detail, it would be desirable to have a cell in which rapid measurements could be made. A cell for this purpose has been designed and built. Measurements are presented for acetonitrile, dimethylformamide, and nitrobenzene.

II. THEORY OF ELECTROOSMOSIS

Electroosmosis is the phenomena of a fluid moving with respect to a solid wall when a potential has been applied across the fluid. Ruess first observed this phenomena in 1808 which makes electroosmosis one of the first electrochemical effects to be observed. Extensive experimental studies were carried out later by Wiedemann[1] and Quincke.[2] Quincke[3] in his studies first suggested that a streaming potential should exist between the wall and the fluid. The streaming potential is the reverse of electroosmosis. Electroosmosis is expressed in terms of velocity of flow or in volume moving per unit time. For our purposes volume will be used.

The theory of electroosmosis has been treated extensively by Helmholtz,[4] Lamb,[5] Smoluchowski,[6] and Per-

Figure 1: Cell Designed for Electroosmosis Measurements

SCALE:
1 inch = ½ inch
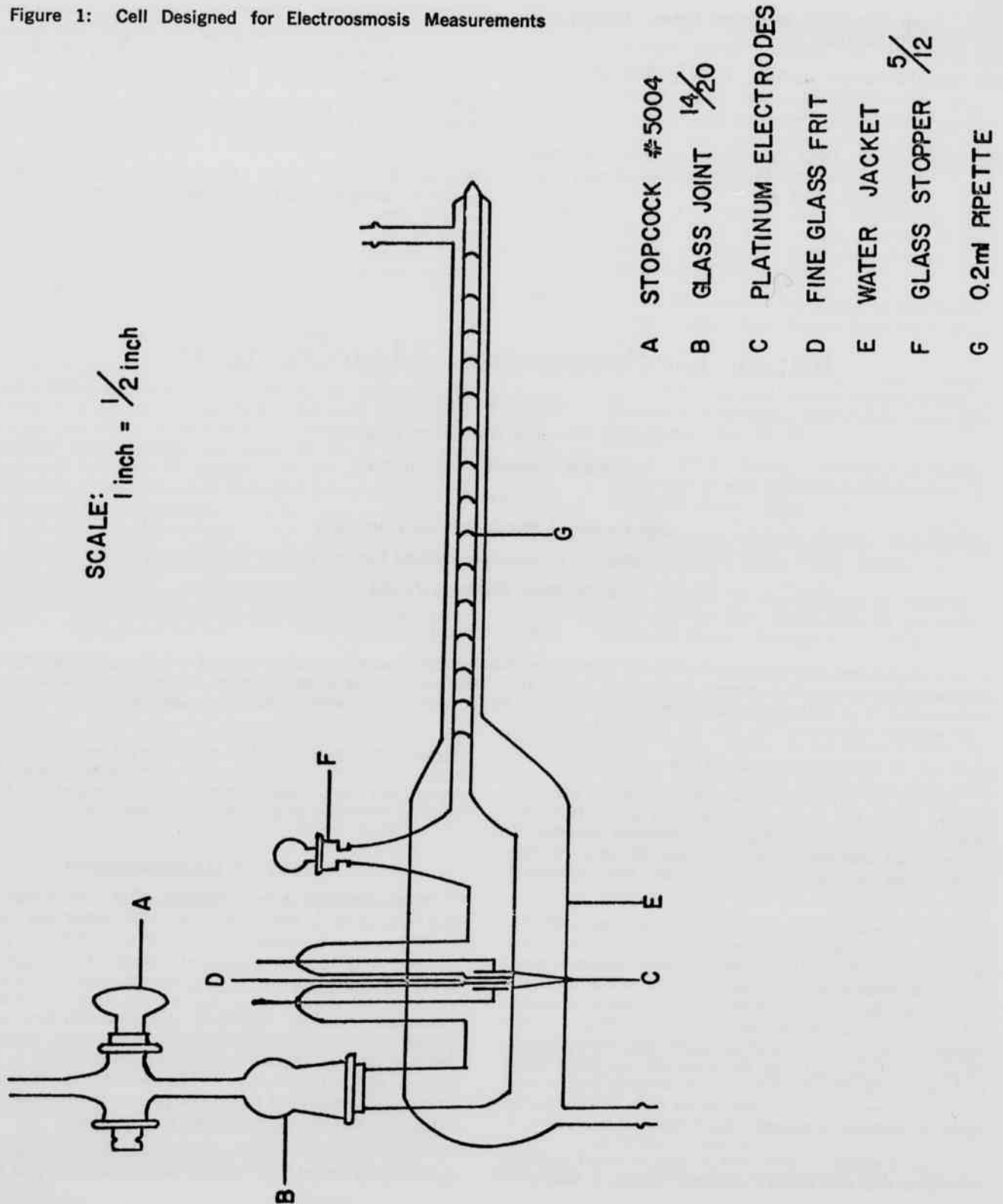
A   STOPCOCK #5004

B   GLASS JOINT ¹⁴⁄₂₀

C   PLATINUM ELECTRODES

D   FINE GLASS FRIT

E   WATER JACKET

F   GLASS STOPPER ⁵⁄₁₂

G   0.2ml PIPETTE

rin.[7] All of the treatments arrived at basically the same expression although some considered a single capillary[4] and other considered a porous plug[6] separating the electrodes. The derived expression is

$$V = \frac{\epsilon \zeta I}{4\pi\eta\lambda} = \frac{\epsilon \zeta AE}{4\pi\eta 1}$$

where V = volume of fluid in cc moved per second

ϵ = dielectric constant of the fluid

I = current

E = applied potential in ESU units

η = viscosity of the fluid in poise

λ = specific resistance of the fluid (includes geometry of the cell)

A = cross-sectional area of the capillary in cm[2]

1 = distance between the electrodes in cm

ζ = "zeta" potential for the electric double layer as a condenser in ESU units

Since A and 1 are difficult to measure the first form of the equation is generally used. The dielectric constant is near impossible to determine since it would not be for the bulk liquid but just for the double layer which cannot be measured. Since most authors fail to state what they used for ϵ in calculating ζ, lists of these potentials are usually worthless. For this reason it has been suggested[9] that a new term called the Gouy be defined as:

$$G = \zeta\epsilon/4\pi\eta$$

This new term would lump all of the characteristics of the fluid into one constant which could be more easily compared.

The temperature dependence of V is extremely complex since the dielectric constant is proportional to e^{-LT}

where T is in degres Kelvin and L is an empirical parameter; η is proportional to $e^{1/RT}$ where R is the gas constant; and λ is directly proportional to temperature. In addition to these temperature dependences the co-efficients of thermal expansion of both the material of the cell and the considered fluid must be taken into account. It appears that it would be best to measure this temperature dependence of V for any considered system.

III. CELL DESIGN

Since the volume of fluid moved in a unit time is

the important measurement for electrochemical systems using electroosmosis, a cell has been designed for rapidly obtaining these measurements.

Many cells have been designed and used[9][11] in the past fifty years. However, most of these cells have been very elaborate pieces of glassware[9] and use porous plugs[10][11][16][18][19] that are difficult to prepare. In addition, most of these cells require a considerable length of time for measurements. Despite the elaborate designs most of these cells were not made in a way to allow easy temperature control. As a result of this design feature, many electroosmotic measurements have been made at room temperature.

In Figure 1 is shown our design for a cell that will allow rapid measurements in a temperature controlled environment. The volume measurements are obtained by measuring the volume moved in the calibrated 0.2 ml pipette (G) as a function of time. The electrodes (C) are bright platinum discs of about one centimeter diameter and placed about 2 millimeters on each side of a fine glass frit plug (D). The starting plug is a medium frit but after heating by the glassblower during the preparation of the cell, the final plug is about a fine frit.

The cell is contained in a glass jacket through which a liquid from a thermostated bath can be pumped. The temperature of the cell can be monitored by a thermocouple. This temperature controlled method can be improved by wrapping the cell jacket with an insulating tape. A range of -20 to +100° C can easily be obtained with this temperature control with a precision of 0.1° C.

A stand to allow for easy leveling and obtainment of a reproducible position was made to hold the cell. This holder was made out of Lucite to prevent a large heat loss to the cell holder, but any nonconducting material could be used.

IV. MEASUREMENTS

The cell has been used for measurements on three liquids that were being considered for relays, acetonitrile, dimethylformamide, and nitrobenzene. All of these liquids were reagent grade and were not further purified.

The measurements were made at 25° C using a bath with a 50-50 volume percent ethylene glycol-water mixture. The liquid was pumped through the cell jacket using a 1/35 hp, 3000 rpm centrifugal pump. The temperature of the jacket was monitored with a copper-constantan thermocouple with a melting ice reference and a K-3 potentiometer.

D.C. voltages of 25, 50, 75, and 100 volts were used for the measurements. These voltages were produced with a Lambda model C-480M regulated power supply.

To cancel out any forces besides those of electroosmosis, measurements were made with the fluid moving in both directions and then these times were averaged. All measurements were made for 0.1 ml volume moved and the time was obtained with a stopwatch.

The results of these measurements for acetonitrile, dimethylformamide, and nitrobenzene are presented in Table I. Each value in Table I is the average of 10 measurements. The results are presented for volume moved as this was the parameter of interest and is a common presentation. The Gouy is also calculated. The value for the streaming potential, 0.0896 volts, agrees well with the literature value of 0.0834 volts.[22]

From Table I it can be seen that even with a fluid that moves as slow as nitrobenzene only six minutes are required for a measurement in our cell (0.1 ml volume moved). Of course, this excludes set up time which is about 30 minutes including temperature equilibration time.

TABLE I

Volume of Liquid Moved and $\zeta \varepsilon / 4\pi \eta$ from Electroosmosis at Various oltages for Acetonitrile, Dimethylformamide and Nitrobenzene.

Compound	cc/sec/volt	Voltage	$\zeta \varepsilon / 4\pi \eta$ (Gouy)
Acetonitrile	1.98×10^{-4}	25	1.98×10^{-3}
Acetonitrile	2.17×10^{-4}	50	2.17×10^{-3}
Acetonitrile	2.26×10^{-4}	75	2.26×10^{-3}
Acetonitrile	2.27×10^{-4}	100	2.27×10^{-3}
Dimethylformamide	5.92×10^{-5}	25	5.92×10^{-4}
Dimethylformamide	6.24×10^{-5}	50	6.24×10^{-4}
Dimethylformamide	6.30×10^{-5}	75	6.30×10^{-4}
Dimethylformamide	6.37×10^{-5}	100	6.37×10^{-4}
Nitrobenzene	1.12×10^{-5}	25	1.12×10^{-4}
Nitrobenzene	1.27×10^{-5}	50	1.27×10^{-4}
Nitrobenzene	1.30×10^{-5}	75	1.30×10^{-4}
Nitrobenzene	1.37×10^{-5}	100	1.37×10^{-4}

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