

Zeta potential determination of pulp suspensions using streaming potential measurements

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ABSTRACT

An apparatus for measuring the zeta potential of pulp suspensions has been described and tested. The results have been compared with the zeta potential measured using a widely accepted laboratory instrument zeta meter 3+ working on the principle of micro-electrophoresis. The agreement between the two systems is found to be quite good.

INTRODUCTION

Zeta potential of a colloidal suspension is an important parameter which provides valuable information regarding its behavior in terms of stability. The concept has been applied for studying the stability of diverse areas including paper making (1,2). Ions carrying opposite charge (counter ions) gather around a charged particle in the suspension. With these counter ions firmly adhering to its surface, the potential of a charged particle with reference to the bulk of the suspending liquid is known as zeta potential. Depending upon the value of this potential, particles in the suspension may settle or remain in suspended state.

Measurement of streaming potential is one of the methods used for the determination of zeta potential of a suspension. The streaming potential technique is based on the principle of electro-osmosis, whereby the charged particles in a suspension are not allowed to move but the liquid is forced to move, as a result of which a voltage difference is developed across the porous plug blocking the movement of particles (3,4). In this article, an apparatus has been discussed and used for the measurement of streaming potential of pulp suspensions. Zeta potential of the specimen suspension is calculated using the streaming potential

data. The values of zeta potentials so determined for pulp suspensions have been compared with those measured using a laboratory instrument zeta meter 3+ working on the principle of micro-electrophoresis. The agreement between the two systems is quite good.

STREAMING POTENTIAL

Streaming potential is defined as the difference in voltage across a porous plug or a capillary tube through which a suspension is forced to flow by an externally applied pressure difference. The phenomenon can be thought of as opposite to the phenomenon of electro-osmotic pressure. Liquid flowing through the plug carries with it the mobile part of the double layer (layer of counter ions around a charged particle) with its charge. As a result of which, counter ions gathering around charged particles in the suspension, move with the liquid and a voltage is developed in the direction of the the flow of liquid.

Assuming laminar flow of suspension in a capillary of uniform diameter, the rate of charge i transported through the capillary may be given by the following equation (4) :

$$i = \frac{P D \gamma^2 \xi}{4 \eta l} \quad (1)$$

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Where i represents the current in milliamperes, P represents the externally applied pressure difference across the capillary in Newtons per square meter, D represents the dielectric constant of the suspension in Farads per meter, r represents the radius of the capillary in meters, G represents the zeta potential of the suspension in millivolts, η represents the viscosity of the suspension in Newtons second per square meter, and l represents the length of the capillary in meters.

The above equation is valid for the case when all the liquid moves with the same velocity in the capillary, which is true only when the thickness of the double layer is much smaller than the capillary diameter. In practice the above condition does not pose any problem, as the thickness of the double layer is of the order of $0.1 \mu m$; which is very small as compared to normal capillary dimensions.

Current conducted through the capillary due to streaming potential E_s may be written as

$$i = \frac{E_s (A \lambda + S \lambda_r)}{l} \quad (2)$$

where E_s is in millivolts, λ represents the specific conductivity of the liquid in mhos per meter, λ_s represents the excess conductance in mhos along the surface of the capillary as a consequence of accumulation of ions in the double layer. For dilute solutions, λ_s may be of the order of same magnitude as the conductance through the bulk of the liquid. A represents the cross-sectional area of the capillary in meters square, while S represents the circumference of the capillary in meters.

By rewriting Eqn. (2), we obtain

$$i = \frac{E_s (\pi r^2 \lambda + 2 \pi r \lambda_s)}{l} \quad (3)$$

At steady state, the charge transported by the moving double layer will be balanced by the current conducted through the liquid as a result of streaming potential. Therefore, comparing Eqns. (1) and (3) and by rearranging the terms, we get

$$\xi = \frac{4 \pi \eta E_s (\lambda + 2 \lambda_s/r)}{P D} \quad (4)$$

In case, the conductance determining the conduction current is mainly dependent on the bulk conductivity of the liquid, surface conductance λ_s along the capillary may be assumed to be zero and Eqn. (4) may be written as

$$\xi = \frac{4 \pi \eta E_s \lambda}{P D} \quad (5)$$

For an incompressible liquid, the above equation may be applied to capillary of arbitrary and non uniform cross-sectional area. As a porous plug can be represented by a parallel combination of capillaries of non-uniform cross-section, the above equation holds good for porous plugs also, provided the pore diameters are large compared to double layer thickness.

Eqn. (5) can be used to calculate the zeta potential of a suspension if the streaming potential developed across a capillary or a porous plug as a result of known externally applied pressure difference is measured.

MEASUREMENTS

Apparatus

The apparatus for measuring streaming potential of pulp suspensions is as shown in Fig 1. It consists of a glass tube fitted with a disc plug made of porous glass. The pore diameters of the plug are reasonably uniform and may vary anywhere between 90 to 150 microns. The plug is non corrosive and is reusable. The tube is connected with rubber tubing to two conical flasks A and B for holding the specimen. A vacuum

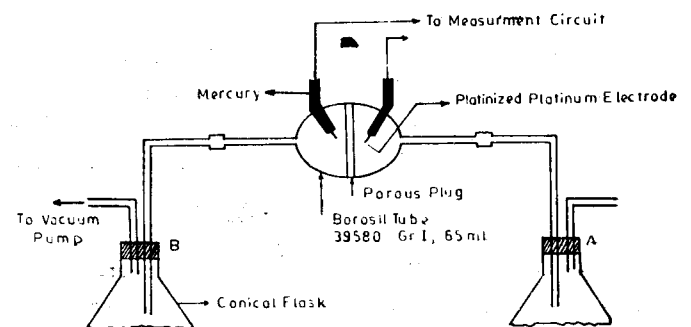


Fig. 1—Apparatus Used for Observing Streaming potential.

pump is connected to either flask A or B depending upon the direction in which the flow of specimen is required in the glass tube. The pump creates vacuum upto 550 mm of Hg below atmospheric pressure. Which can be adjusted any where between 550 to 100 mm using a bleed valve.

Wire electrodes made of platinum are fixed at equal distance from the porous plug for measuring potential across the plug. For ensuring intimate electrical contact between the electrodes and the fluid and to reduce electrode-fluid interfacial capacitance, electrode surface area must be increased by making them rough and porous (5). This is done by platinizing the electrodes i.e. electroplating them with platinum to form an uneven, spongy surface on electrodes, known as platinum black. The platinization is carried out by filling the glass tube with platinizing solution (3 gm. of platinum chloride, 0.03 gm. of lead acetate and 100 ml. of distilled water) and passing small d. c. current through the electrodes for about 15 minutes, the direction of current being reversed every half minute till a black and velvety coating appears on the electrodes (6). To remove the last traces of platinizing liquid and occluded chlorine, the electrodes and the tube are thoroughly cleaned with dilute sulfuric acid and warm distilled water before the apparatus is used for measuring streaming potential. Connections to the platinum electrodes are made through mercury filled tubes holding the electrodes.

The use of bright electrodes in place of reference electrodes puts a restriction on the circuit used for measuring the potential. The circuit should draw almost negligible current from the electrodes (7). In addition to this, since the value of potential may be small, the streaming potential signal may need to be amplified. Therefore, an amplifier circuit satisfying the above requirements has been designed for use with the above apparatus and is as shown in Fig. 2. The circuit makes use of a high performance operational amplifier (IC 7650S) (8). The opamp is chopper stabilized and offers exceptionally low input offset voltage and is extremely stable with respect to time and temperature. The maximum input current drawn by the opamp is only 10^{-11} amperes. The gain of the circuit is five. Voltage at the output of the amplifier is measured by connecting a sensitive digital voltmeter.

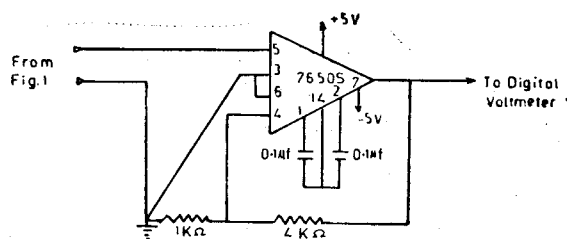


FIG. 2.

High Input Impedance Amplifier.

For making measurements, the specimen is taken in flask A and a pressure difference is created across the porous plug by applying a constant vacuum at flask B with the help of the vacuum pump. Voltage is measured when the specimen is flowing through the porous plug. After this, vacuum is released and the voltage is measured again, with liquid stationary in the tube. The difference between the two voltage readings thus taken divided by the two voltage reading thus taken divided by the gain of the circuit represents the streaming potential of the specimen suspension.

Sample Preparation

Measurements were made on two types of commercial bleached pulps i.e. hardwood (100% Eucalyptus) pulp and a mix of long and short fiber (70% Eucalyptus, 18% Bamboo and 12% Pine) pulp. These pulps were taken from industry, air dried and stored. For studies, (—) 70 fraction of 0.3% consistency samples were prepared (Reasons for the use of (—) 70 fraction have been detailed in an earlier publication [9]).

To prepare slurry of 0.3% consistency, the pulp was soaked for few hours in distilled water and then disintegrated. Consistency of slurry was measured using filter paper and was corrected to exact value of 0.3%. The slurry was then divided into 500ml samples. Predetermined amount of electrolyte solutions (Poly aluminum chloride grade 18/5 from Grasim Industries Ltd.) were added in these samples. After adequate stirring, the samples were subjected to fractionation on Dynamic Retention Jar Mark 1V using stainless steel 70 mesh wire. Same samples were used for investigations on Streaming potential apparatus and Zeta Meter 3+.

Results

Fig. 3 and 4 represent the curves showing nature of zeta potential with variation in electrolyte (PAC 18/5) dosing. The zeta potential has been calculated using the data taken on Streaming potential apparatus and making use of Eqn. 5. Zeta potential values as obtained using the Zeta meter are also plotted. It is evident from the figures that although there is a difference in the values of zeta potential obtained by the two methods, the nature of curves is identical. The observations made on two commercial pulps, thus confirm the interrelationships between the two methods and the versatility of the apparatus.

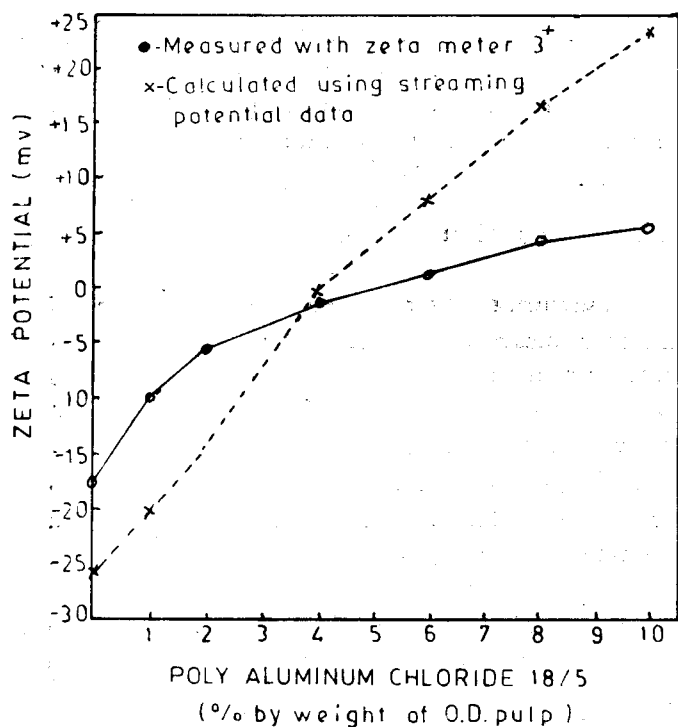
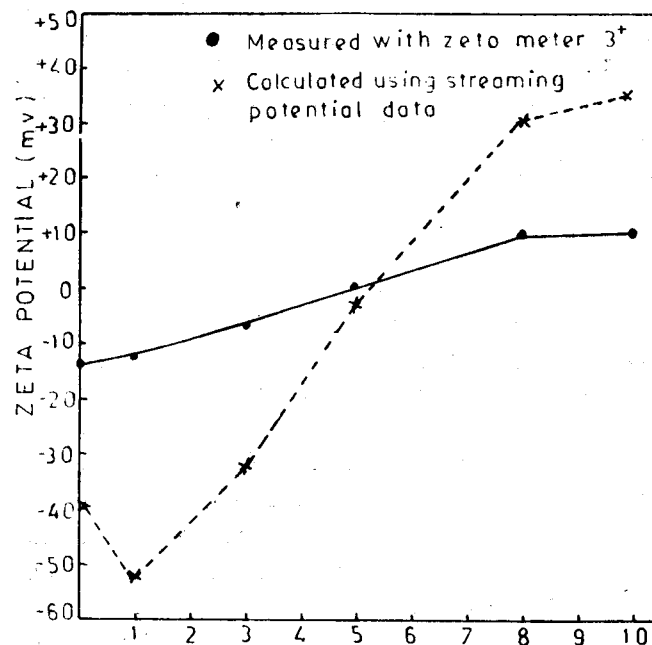


FIG 3 ,

Curves Showing Nature of zeta Potential for Commercial Bleached Hardwood (100% Eucalyptus) Pulp with Variation in Electrolyte (PAC) Dosing Using Streaming Potential Measurements and Zeta Meter.



POLY ALUMINIUM CHLORIDE 18/5
(% by weight of O.D. pulp)

Fig. 4—Curves Showing Nature of Zeta Potential for Commercial Bleached Mix of Long and short Fiber (70% Eucalyptus, 12% Pine, 18% Bamboo) Pulp with Variation in Electrolyte (PAC) Dosing Using streaming Potential Measurements and Zeta Meter.

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