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Original Scientific Paper

## Electrokinetic Studies in Disperse Systems. VI. A Modification of Apparatus and Techniques for Streaming Current Measurements

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The method originally employed by Hurd & Hackermann to measure streaming currents on single capillaries has been modified for measurements on porous diafragms of precipitates. An application of microvolt amplifiers and pressure transducers in connection with chart recorders to record the streaming current — pressure relation is described.

Measurements of electrokinetic potentials (EKP) of porous diafragms have often been performed using either electroosmotic or streaming potential techniques.<sup>1-6</sup> The latter have been successfully employed in solutions of low electrolyte concentrations (up to  $10^{-2}M$ ) using high impedance electrometer-amplifiers.<sup>4,6</sup> With streaming potentials of several tens or hundreds of millivolts this technique presents little difficulty. At high conductivity of the liquid flowing through the diafragma the measured potentials are very small, and it is more convenient to measure the streaming current. Both techniques render the same information on the state of the electrochemical double layer,<sup>7</sup> the choice between them being a matter of the required accuracy. High impedance electrometers are of low potential sensitivity. On the other hand highly stable microvoltmeter amplifiers are obtainable, the input impedance of which is however, seldom higher than a few megohms. Hurd and Hackermann,<sup>8</sup> following an old idea of Eversole,<sup>9,10</sup> were the first to apply this type of instruments for streaming current measurements at low external shunting resistance. However, they limited their investigation to metallic single capillaries being only concerned with measurements of streaming currents in distilled water (low conductivity liquid).

Measurements of EKP of silver iodide in solutions of intermediate concentrations were described in a series of papers.<sup>6,13,14</sup> As the problem of measurements of EKP in high concentrations of electrolyte arose it was considered worth to elaborate experimental conditions of streaming current measurements on porous diafragms.

### EXPERIMENTAL

#### *The streaming cell*

The cell was a further development of previous ideas<sup>6</sup> (Fig. 1). Uni-directional flow of liquid was considered satisfactory since no indication of asymmetry effects has been quoted in the literature.<sup>3,4,6,10,11</sup> The cell consists of an 8 mm

outer diameter glass tube ending on both sides in B7 ground glass sockets. Powdered and sieved glass (40–60 Mesh portion) is brought into the tube and sintered slightly on a small gas flame. With a frit of adequate porosity (which requires a little experience), the rest of the glass is rejected, and the frit is ground by scratching it to a thickness of 2 mm. After the cell has been thoroughly washed a suspension of the material under test is brought into the tube and allowed to

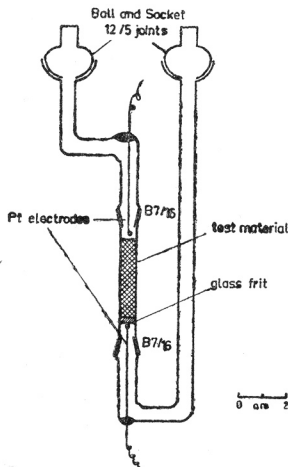


Fig. 1. The streaming current cell. Note the close positioning of platinum wire electrodes to the ends of the diafrgm.

settle onto the diafrgm. Suction is applied to form the diafrgm to a compact size. Reproducible diafragms are readily obtained by controlling the amount of material brought into the cell and applying the suction under controlled vacuum. Care is taken to form the diafragms of equal heights in successive experiments. Also the platinum wire electrodes should just touch the upper end of the diafrgm.

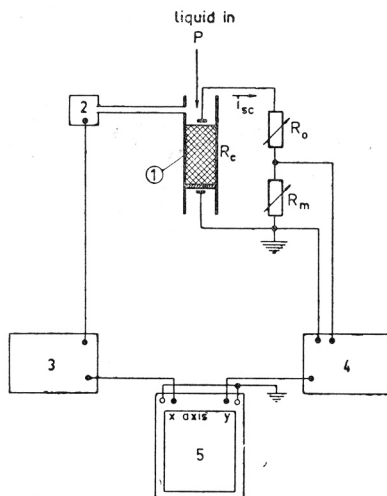


Fig. 2. The experimental set-up for measurements of streaming currents (1) the cell, (2) the pressure transducer with (3) the amplifier, (4) the microvoltmeter amplifier, (5) the X-Y recorder.  $R_c$  denotes the effective resistance of the cell,  $R_o$  is the outer shunting resistance in series with the measuring resistance  $R_m$ .

With the diafragm formed the cell is assembled. The diafragm tube is joined to the electrode holder with B7 cones and then to the reservoir of fluid via ball and socket joints. A volume of several ml. of liquid is pressed through the diafragm before making measurements, to attain streaming equilibrium. In all experiments suspensions equilibrated with the mother liquor were used for the diafragms. A total volume of 100 ml. of solution was needed for the measurement, including free liquid conductivity.

Fig. 2 shows the principal scheme of the apparatus. The cell (1) is shown connected to a reservoir of liquid and a pressure transducer (electric manometer-Sanborn Type 267B differential transducer). The electric signal indicating the applied pressure is amplified and applied to the Y axis of an X-Y recorder or a strip chart recorder (time basis 2 in./min or faster). The electrodes of the cell are externally connected by resistances  $R_0$  and  $R_m$ . The streaming current produces a voltage drop over the precision measuring resistance  $R_m$ . The amplified voltage (Leeds and Northrup D.C. Microvolt amplifier) is applied to the X axis of the X-Y recorder, or to another strip chart recorder. The measurements were performed by applying short pulses of liquid at constant pressure, or by a continuous increase of pressure with a simultaneous recording of the potential. Pressures of 7.5 to 35 cm. of mercury were applied in each measurement. The straight line portions of the dependence of voltage on pressure were taken into calculations.

## RESULTS

Electrokinetic potentials were calculated by the expression derived on the basis of the Helmholtz-Smoluchowski equation:<sup>1,8</sup>

$$\zeta = (4 \eta / D) (i/P) (l/r^2) \quad (1)$$

$l$  denotes the length and  $r$  the radius in the case of single capillary, where these can be measured. In the case of porous diafragms the mean  $l/r^2$  was calculated from the measured electrical resistance of the diafragm and the free liquid.

$$l/r^2 = R \times \kappa \times \pi \quad (2)$$

Thus

$$\zeta = (4 \eta / D) (i/P) (R\kappa\pi) \quad (3)$$

Taking  $\eta = 0.01$  poise,  $D = 80.4$ , and with all the CGS conversion factors for the electrical entities one obtains:

$$\zeta = 1.06 \times 10^8 (i/P) R\kappa\pi \quad (4)$$

$\zeta$  is in mV. provided  $i$  is expressed in Amperes,  $P$  in cm. of mercury,  $R$  in Ohms and  $\kappa$  in  $\text{Ohm}^{-1} \text{cm}^{-1}$ .

Conversely, the same result is obtained if the streaming potential is computed from the streaming current by

$$E = i_{SC}(R_c + R_0 + R_m) \text{ if } R_c \geq R_0 + R_m \quad (5)$$

and

$$\zeta = (4\pi\eta / D) (E/P) \cdot \kappa \quad (6)$$

$$\zeta = 1.05 \times 10^5 \times (E/P) \cdot \kappa \quad (7)$$

where  $E/P$  is the streaming potential increment in mV/cm Hg.

It should be noted that for  $i/P$ , as for  $E/P$ , the mean value of several measurements was taken. The linear dependence was seldom found to be a line through the origin. Several reasons are cited for this observation.<sup>4,12</sup>

Fig. 3 shows the results of the measurements obtained for different materials and various values of the external shunting resistance. In all cases there is a portion in which the current is independent of the external shunting resistance when the latter is lower, or of the order of the cell resistance. From the comparison of data obtained by Hurd and Hackerman<sup>8</sup> for single capillaries of silver metal and those for silver iodide and quartz powder, it can be shown that the described technique is readily applicable to the either system.

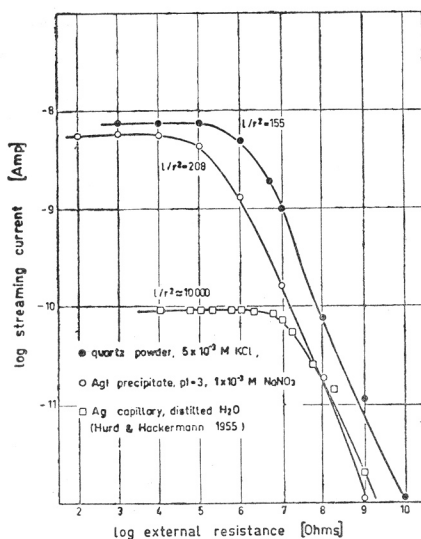


Fig. 3. Log. streaming current vs. log. external shunting resistance for quartz powder (circles), silver iodide (full points) and silver metal capillary (squares).

Finally, there is the question of interpretation of EKP. In a series of previous papers<sup>6,13,14</sup> the electrokinetic potential was used as a relative indicating parameter showing the influence of the composition of the liquid phase on the surface of the solid phase. In this manner the influence of certain ions can be measured relative to an initial state in the absence of this particular species in the same system. This approach to electrokinetic phenomena of disperse systems in solutions has been successfully applied to the study of ion exchange equilibria in the silver iodide-aqueous solution<sup>15</sup> system and in the system uranium oxide-aqueous solution.<sup>16</sup>

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### IZVOD

#### Elektrokinetičke studije u disperznim sistemima. VI. Modifikacija aparata i tehnike za mjerenja struja strujanja

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Opisana je metoda i tehnika mjerenja struja strujanja za porozne diafragme od netopivih taloga. Metoda se sastoji u mjerenju pada napetosti preko otpora u krugu obaju elektroda, kroz koji teče struja uzrokovana strujanjem tekućine. Prikazana je izvedba ćelije za mjerenje, kao i uređaja koji vrši registraciju ovisnosti struje o pritisku na X—Y pisac. Mjerenja na prašku kvarca i talogu AgJ uspořeđena su sa podacima koji su dani u literaturi za kapilare.

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