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Electrokinetic Studies in Dispersed Systems. I. A Streaming Potential Device

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A streaming potential device for work with dispersed material is described. The use of a vibrating condenser electrometer-amplifier in connection with a paper strip recorder gives the possibility to perform measurements in short time and with small volume of liquid. Statistical analysis of the results on quartz particles of three different sizes in KCl solutions (1×10^{-5} to 5×10^{-3} *N*) is given. The determination of the ζ-potential with this device and experimental technique can be performed with a standard error of about 5%.

INTRODUCTION

When a liquid is forced through a porous plug a potential difference, the streaming potential, arises between both sides of the plug. This potential is given by the equation[1]

$$\Delta E = \frac{\varepsilon \zeta P}{4 \pi \eta \varkappa} \tag{1}$$

in which ΔE is the potential difference measured by two unpolarisable electrodes, ε the dielectric constant, P the applied pressure, η the viscosity and $\varkappa$ the conductivity of the liquid within the pores of the plug. The ζ-potential is a magnitude related to the hypothetical potential drop within the diffuse double layer according to Stern. The value of the ζ-potential is uncertain to some extent. The uncertainties arise from the nonmeasurable values: the dielectric constant within the double layer, the viscosity of the liquid in the slipping plane and the additional conductivity, the »surface conductivity«[2].

It is usual to insert bulk values for the first and second term in computations of ζ, and make corrections for the surface conductivity only. Both mathematical and experimental methods were proposed[3,4]. Surface conductivity plays an important role in dilute solutions only, and disappears in concentrations of 10^{-1} *N* of strong electrolytes[5], but at this concentration the electrokinetic phenomena are to small to be accessible to measurement. Streaming potential measurements are possible at the most up to a concentration of 10^{-2} *N*, but with considerable experimental error.

There are in the literature some more elaborate expressions for the calculation of ζ-potentials, none of them beeing fundamentally different. In the

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present paper expression (1) was used because many of the results on streaming potential measurements on quartz were expressed in terms of ζ calculated by this expression. Thus comparison is possible.

The streaming potential method has advantage over electroösmosis for certain systems because no external electrical field is applied by which changes in the system may be made. It is essential, however, to make curentless measurements of the potential difference. Using high resistance circuits and performing measurements in short time it is possible to achieve reproducible conditions.

EXPERIMENTAL

Apparatus

Fig. 1 illustrates the streaming potential cell. It consists of two flasks (about 75 ml.), the »plug«-tube and a U-joint. The right hand flask has attachments for gas inlet and one of the electrodes, the other flask for the thermometer, the solution outlet and the other electrode. The plug-tube has a coarse grain sintered glass disc above which two bright platinum electrodes are sold into the walls. The plug-tube is constructed as a conductivity cell; it can be stoppered on both sides and immersed into a constant temperature bath. The parts of the cell are connected together by ground glass joints. The plug is formed by pouring the suspended material in small portions onto the glass disc in the plug-tube. The plug remains always immersed in solution. A height of the plug of about one cm. is considered satisfactory. The influence of the sintered glass on the streaming potential was found to be negligible. The results were the same when the sintered glass disc was changed for a sheet of filter paper on a perforated plastic (Perspex) support. The plastic was not used since it was found to cause difficulties in rigorous cleaning.

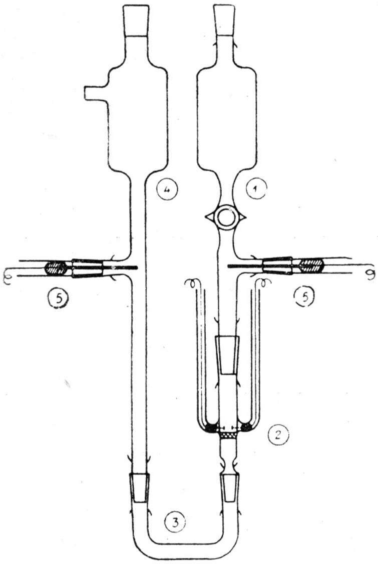

Fig. 1. The streaming potential cell. (1) The flask with the stopcock and attachements for gas inlet (top) and the electrode (side arm). (2) The plug tube with the sintered glass disc and the sold-in platinum electrodes. (3) The U-joint. (4) The flask with attachements for electrode (side arm) and thermometer (top). (5) The Ag/AgI electrodes.

The electrodes in the side arms were silver sheet coated electrolytically with silver iodide.

Fig. 2 shows the whole assembly with the arrangement for constant pressure (the 5 liters bottle), the mercury manometer and the tubing. The electrical circuit is shown in the lower part of Fig. 2 in block sketch. The Ag/AgI electrodes in series with a potentiometer (Precision Three Dial D. C. Potentiometer of the Doran Instr. Co.) are connected to the terminals of a vibrating condenser electrometer (Vibron 33 B Electrometer of the Electronic Instr. Co.). The D. C. output of the electrometer is applied to a paper strip recorder (Type S/H of the C. P. Goerz, GMBH). The total resistance of the electrical circuit, due to the high input resistance of the electrometer, exceeds 10^{13} Ohms. Thus the condition of currentless measurement of streaming potential is fairly well established. The sensitivity of the electrometer can be selected from 10—1000 mV full scale deflection. The output is 1 mA D. C. on all ranges. The recorder has a range of 1 mA, a setting time of 1 sec. and a chart width of 120 mm. The maximum sensitivity with reasonable stability attained was 0.25 mV/mm. (range 30 mV f. s. d.).

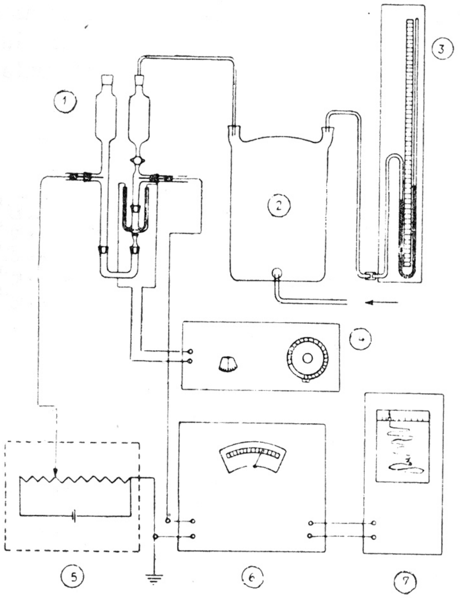

Fig. 2. The streaming potential device. (1) The cell. (2) The constant pressure balast bottle (an arrow is showing the gas inlet). (3) The mercury manometer. (4) The conductivity bridge. (5) The potentiometer. (6) The electrometer-amplifier. (7) The paper strip recorder.

The pressure is applied to the cell by connecting the tube from a gas (usually nitrogen) tank through the balast bottle. The flow of liquid is started by opening the cell stopcock. The potential measured on the electrometer is simultaneously recorded on the chart of the recorder. When the flow of the liquid is stopped an accurately measured potential of the same order of magnitude is applied by the potentiometer and recorded for calibration purpose. By repeating the procedure of measurement and calibration it is possible to elliminate all nonlinear responses of the instruments. A single measurement can be made in a few seconds and several with the same filling of liquid.

Similar devices have been described[4,6], but the present has advantages in simplicity of work, in the need for a much smaller volume of the liquid and in the speed of recording.

After measurements of the streaming potential the cell is disconnected, the plug-tube with the plug inside stoppered and immersed into a constant temperature bath held at 20.0 ± 0.05°C. The conductivity measurements were made just after those of the streaming potential. Readings were taken on a 1000 cycle conductivity bridge

(Conductivity Bridge Cat. No. 43923 of the Cambridge Instr. Co.) with a precision of 0.5%. The standard error of three repeated determinations was about 3%.

Materials used

The quartz under test was Merck acid washed A. R. grade. It was crushed in an agate mortar and sieved through standard sieves (U. S. standard). Three fractions of 100—200, 200—270, 270—325 mesh were taken, washed with concentrated nitric acid, with redistilled water till the filtrate showed *p*H=6, and stored under redistilled water. *p*H was ocassionaly controled but no change was found.

Potassium chloride was A. R. quality (Pliva, Zagreb). Redistilled water was used throughout (specific conductivity less than 2×10^{-6} mhO/cm.).

RESULTS AND DISCUSSION

The accuracy of the measurements with this device was statistically determined by measuring streaming potentials of quartz particles plugs. From each fraction a plug was formed and solutions of potassium chloride from 1×10^{-5} *N* to 5×10^{-3} *N* were used. For each concentration of potassium chloride and fraction of quartz seven points at different pressures were recorded. Each single point of the recorded potential is the arithmetic mean of five measurements. A typical plot of the streaming potential in mV *vs.* the applied pressure in cm. of mercury is given in Fig. 3.

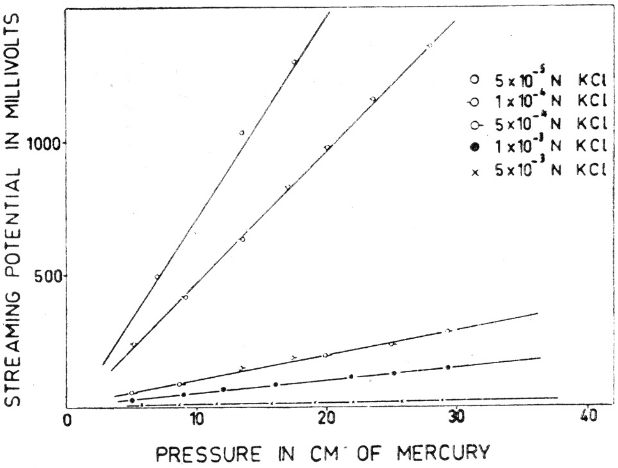

Fig. 3. A typical plot of streaming potential in millivolts *versus* the applied pressure in cm. of mercury for a plug of quartz particles in various concentrations of potassium chloride.

As it is obvious the plots are lines, but not through the origin. The linearity is maintained from about 5 to 30 cm. of mercury. The plots have the general form of the regression equation

$$y = bx + a \tag{2}$$

where $y = E$, and $x = P$. b is the regression coefficient of y upon x. The term a varies from plug to plug. ζ-potentials were computed from the general equation (1) by insertion of $\eta = 0.009$ poise, $\varepsilon = 78$, the specific gravity of mercury = 13.55 g./cm.^{3}, the gravitational force acceleration = 981 cm./sec..^{2}, b instead of E/P and transforming the electrical units it becomes

$$\zeta = 9.69 \times 10^4\, b\, \varkappa \tag{3}$$

ζ is in mV if b is in mV/cm. of mercury and $\varkappa$ in mhO/cm. To ζ the sign of the »upstream« electrode is given.

In Table I are given successively: the size of quartz particles forming the plug; the concentration of the electrolyte; the regression coefficient of the streaming potential upon pressure and its standard error; the specific conductivity of the liquid inside the plug and its standard error; the last two columns give the per cent relative standard error in b and in ζ. The standard error in ζ was computed by the equation[7]

$$s(\zeta) = 9.69 \times 10^4 \sqrt{[s(b)\,\varkappa]^2 + [s(\varkappa)\,b]^2} \tag{4}$$

TABLE I

1	2	3	4	5	6	7	8	9	10
Mesh No. of quartz	Conc. of KCl (*N*)	Regression coefficient *b*.	Standard error in *b* S. E. (*b*)	Spec. cond. $\varkappa \times 10^5$	St. error in $\varkappa$ S. E. ($\varkappa$)	ζ-potential in mV	St. error in ζ S. E. (ζ)	Relative st. error in *b* in %	Relative st. error in ζ in %
100—200	5×10^{-5}	65.0	1.5	1.32	0.06	83.0	4.2	2.3	5.1
	1×10^{-4}	39.9	1.7	2.06	0.08	78.5	4.4	4.3	5.6
	5×10^{-4}	8.12	0.12	8·30	0.21	65.4	1.9	1.5	2.9
	1×10^{-3}	3.91	0.25	15.2	0.3	57.5	3.8	6.4	6.6
	5×10^{-3}	0.318	0.018	71.3	0.4	22.2	1·3	5.7	5.9
200—270	5×10^{-5}	76.2	1.4	1.27	0.07	93.6	5.5	1.8	5.9
	1×10^{-4}	49.8	0.4	1.99	0.06	95.7	3.0	0.8	3.2
	5×10^{-4}	8.83	0.30	8.47	0.17	72.5	2.9	3.5	4.0
	1×10^{-3}	4.72	0.17	14.8	0.3	67.8	2.8	3.6	4.1
	5×10^{-3}	0.656	0.011	72.1	0.4	45.8	0.9	1.7	2.0
270—325	1×10^{-5}	8·65	0.64	0.81	0·02	6.8	0.53	7·4	7.7
	1×10^{-4}	6.48	0.75	1.96	0.05	12.3	1.5	11.5	12.2
	1×10^{-3}	1.88	0.12	14.5	0.3	26.4	2.6	6.4	10.0
	5×10^{-3}	0.0809	0.020	73.2	0.4	5.7	1.4	24.6	24.7
							Mean	4.4	5.1

The values of ζ show a relatively good agreement with the data from the literature[5,8]. With this device and experimental technique it is possible to attain a reproducibility within 5%, which, it seems, is the limit of accuracy in electrokinetic measurements on porous plugs.

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IZVOD

Elektrokinetičke studije u disperznim sistemima. I. Uređaj za mjerenje potencijala strujanja

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Opisana je aparatura za mjerenje potencijala strujanja u disperznim sistemima. Upotrebom elektrometra s vibrirajućim kondenzatorom i registrirajućeg miliampermetra mjerenje se ubrzava, te je potreban manji volumen otopine. Statističkom analizom rezultata dobivenih mjerenjima potencijala strujanja na česticama kvarca triju različnih dimenzija u otopinama KCl (konc. 1×10^{-5} do 5×10^{-3} *N*) ustanovljena je standardna pogreška ζ-potencijala od 5%.

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