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# Electrokinetic Studies in Dispersed Systems. II. An Electroosmotic Apparatus

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A description of an electroosmotic apparatus based on the principle of a micro bubble flow meter is given. Statistical analysis of some results obtained on quartz particles in aqueous and methanolic solutions of potassium chloride is given, the mean standard error beeing about 7%.

## INTRODUCTION

When a potential difference is applied to both ends of a porous plug the electroosmotic transport of the electrolyte solution trough the plug will be observed. The relation between the transported volume of the liquid $V$ and the electric current $I$ is given by Smoluchowsky (i. e. ref.[6] p. 201):

$$V = \frac{\varepsilon \zeta}{4 \pi \eta \varkappa} \cdot I$$

In the equation $\varepsilon$ denotes the dielectric constant, $\eta$ the viscosity and $\varkappa$ the specific conductivity of the liquid within the pores of the plug. $\zeta$ is generally explained as a hypothetical potential drop between a point in the bulk of the liquid and a point inside the electrical double layer, in the »slipping plane«. The $\zeta$-potential obtained by this simple interpretation can serve for the comparison of the measured effects in a certain system with electrolytes of different conductivity, avoiding any theoretical or empirical evaluation of either the »true« or »corrected« $\zeta$-potential. Namely, no theoretical interpretation could as yet be definitely confirmed by a direct experimental method. As to the existing theories some objections have been recently raised and new theoretical approaches suggested[1-7].

Whatever the theoretical significance and the physical meaning of the measured $\zeta$-potential should be, it will be considered here simply as a value proportional to the measured product of the electroosmotic effect and the conductivity of the electrolyte. It represents one of the few experimentally accessible magnitudes, which can be used for the phenomenological elucidation of the electrochemical properties of the double layer between a solid and a liquid phase. Experimental data of this type are needed for the developement and confirmation of any theory of the double layer. In this paper and the papers to follow the $\zeta$ potential is interpreted in the same sense.

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In the present paper an improved apparatus for the measurement of the electroosmotic effect, with a micro bubble flow meter is described and tested. This apparatus was developed from the one used by the senior author in his early investigations of the electroosmotic effect on AgI[8], and which in turn was constructed following the devices described by Briggs, Bennet and Pierson[9], by Fairbrother and Stubbs[10] and by Ghosh and Roy[11]. The improvements of the present device are a large reduction of the amount of material needed to form the plug, a simplification of levelling and adjustment of the apparatus and the possibility of achieving a low current density in the plug, as well as the introduction of a micro buble flow meter.

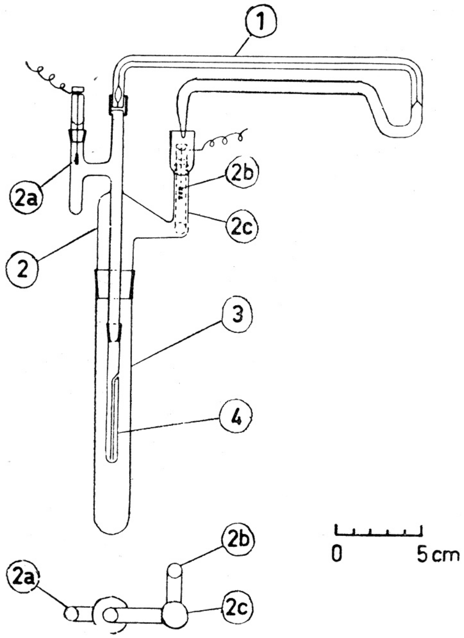

**Fig.** 1. The electroosmotic apparatus: (1) the micro bubble flow meter, (2) the central part, (2*a*) and (2*b*) the electrode sockets with electrodes in cone holders, (2c) the side arm funnel, (3) the larger tube, (4) the coaxial plug-tube.

## EXPERIMENTAL

*The apparatus.* The apparatus consists of 6 parts (Fig. 1): (1) the micro bubble flow meter, (2) the central part with (2*a*) and (2*b*) electrode compartments and electrodes, (3) the larger tube and (4) the coaxial plug tube. The parts of the apparatus are connected by means of the ground glass joints, except for the connection between the flow meter and the inner central part, where a piece of tygon tubing was used.

The electrolyte in the apparatus forms a closed circuit and therefore the speed of flow is independent of the levelling. The speed of flow of the liquid is indicated by the movement of an air bubble in the calibrated capillary. A suitable capillary for this purpose had a calibration value of 2 $\mu$l/cm. A current of a few microampers gave measurable shifts of the bubble in about 30 sec. The capillary has bubble traps on both sides. By pressing the tygon connection the bubble can be brought to any desired starting point in the capillary.

The plug is formed by successive additions of the dispersed material, suspended in the electrolyte solution, into the tube by a dropper. The filled plug tube is then centrifuged at a suitable, controlled speed which depends upon the material and has to be established by experience.

The plug tube with the plug is then attached to the central part of the apparatus and inserted into the larger tube. The apparatus is filled with the electrolyte and the electrodes (silver/silver halide or some other reversible system) in their ground glass cone holders are placed into the proper sockets on the side arms of the central part. The capillary, filled with conductivity water and with the bubble in one of the traps, is attached to the central part by the piece of tygon tubing. The right hand tip of the flow meter is dipped into the electrolyte in the central part of the apparatus in the opening 2c. The apparatus, adjusted in this way, is immersed into a constant temperature bath, and the measurement performed.

About 30 ml. of solution are necessary for one filling of the apparatus. The amount of solid material depends upon its consistency and specific gravity, but in general it does not exceed 0.1 gram.

The measurement is performed in the way that the electrical circuit is switched on with a predetermined current and the movement of the bubble in the capillary measured by a stop watch. Afterwards the current is reversed and the opposite movement of the bubble measured. The mean values of »left« and »right« movement are used in calculation. The current was drawn from a stabilised rectifier of 600 V output and measured by a light-spot microampermeter with an overall accuracy of ± 1.5%.

Conductance measurements were performed in a streaming potential cell (with the plug) as described in the first paper of this series[12].

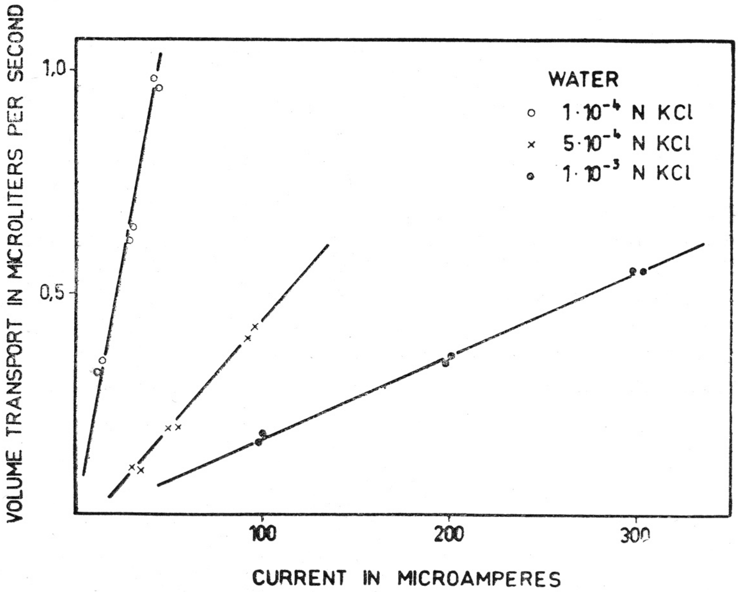

Fig. 2. Typical plots of experimental data: experimental points and regression lines of volume transport upon current strength for the system quartz (200—270 Mesh) — aqueous solutions of KCl.

*Materials used.* The quartz under test was of the same batch as described in the previous paper[12]. The fraction of 200—270 mesh (U. S. standard) was used in this series of experiments.

Redistilled water with a conductivity of less than $2 \times 10^{-6}\ \Omega^{-1}$ cm.$^{-1}$ was used throughout. Analytical grade methanol (Chinoin, Budapest) was distilled through a

Vigreux coloumn of 45 cm. length. The percentages of methanol in the distillate were determined by specific gravity.

Potassium chloride of analytical grade was used without further purification.

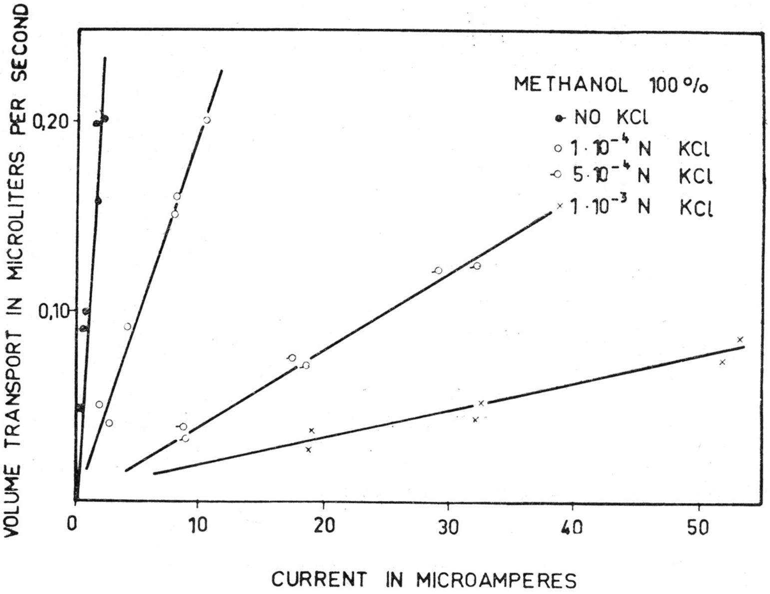

**Fig.** 3. Typical plots of experimental data: experimental points and regression lines of volume transport upon current strength for the system quartz (200—270 Mesh) — 100% methanolic solutions of KCl.

## RESULTS AND DISCUSSION

Volume transports were measured for each plug 6 times at different currents. The measurement was taken as succesfull if a linear dependence of the volume transport in unit time against current was obtained. In accordance with the streaming potential data the plots are lines (see Figs. 2 & 3) of the general type $y = bx + a$, where $b$ is the regression coefficient of $y$ upon $x$ (the current strength taken as the independent variable). $a$ is a constant, varying from plug to plug. Neglecting this fact one can obtain erroneous results.

The $\zeta$-potentials were computed from the expression

$$\zeta = \frac{4\pi\eta}{\varepsilon} \varkappa b$$

by inserting the proper values for viscosity, dielectric constant, conductivity and $b$ (instead of $V/I$ obtained in a single measurement). Transforming the electrical units and reducing the constants into one constant the expression for aqueous solutions at 20°C becomes:

$$\zeta = 1.42 \times 10^5 \varkappa\, b \qquad [\mathrm{mV}]$$

for methanolic solutions at 20°C:

$$\zeta = 1.96 \times 10^5 \varkappa\, b \qquad [\mathrm{mV}]$$

providing $\varkappa$ is expressed in $\Omega^{-1}\,\mathrm{cm}^{-1}$, and $b$ in ml./sec. Amp.

TABLE I

| Conc. of KCl $N$ | Regression coefficient $b$ | Standard error in $b$ | Relative stand. error in $b$ in % | Specific conduct. $\varkappa \times 10^6$ | Standard error in $\varkappa$ | $\zeta$-potential in mV | Standard error in $\zeta$ | Relative stand. error in $\zeta$ in % |
|---|---|---|---|---|---|---|---|---|
| $1 \times 10^{-5}$ | 87.0 | 9.5 | 10.9 | 8.1 | 0.2 | 101 | 11 | 10.9 |
| $5 \times 10^{-5}$ | 41.0 | 4.4 | 10.7 | 15.1 | 0.6 | 88 | 10 | 11.4 |
| $1 \times 10^{-4}$ | 26.5 | 1.1 | 4,2 | 19.9 | 0.6 | 75.0 | 3.9 | 5.2 |
| $5 \times 10^{-4}$ | 4.16 | 0,21 | 5.0 | 88.5 | 1.7 | 56.1 | 2.9 | 5.2 |
| $1 \times 10^{-3}$ | 1.94 | 0,03 | 1.8 | 158 | 3 | 43.5 | 1.1 | 2.6 |
| $5 \times 10^{-3}$ | 0.235 | 0.018 | 7.4 | 721 | 4 | 24.1 | 1.8 | 7.6 |
| $1 \times 10^{-2}$ | 0.102 | 0.005 | 4.5 | 1380 | 7 | 20.0 | 0.9 | 4.5 |
| | | Mean | 6.3 | | | | Mean | 6.9 |

In table I. the following data are given successively: the concentration of KCl; the regression coefficient of volume transport in unit time upon current; its standard and relative standard error; the specific conductivity of the liquid and its standard error; the computed $\zeta$-potential its standard error and its relative standard error, for quartz particles in aqueous solutions of KCl.

TABLE II

| Conc of KCl $N$ | Regression coefficient $b$ | Standard error in $b$ | Relative stand. error in $b$ in % | Specific conduct. $\varkappa \times 10^6$ | Standard error in $\varkappa$ | $\zeta$-potential in mV | Standard error in $\zeta$ | Relative stand. error in $\zeta$ in % |
|---|---|---|---|---|---|---|---|---|
| 0 | 160 | 13 | 8.1 | 2.66 | 0.10 | 83.5 | 7.3 | 8.7 |
| $5 \times 10^{-5}$ | 34.5 | 1.2 | 3.5 | 7.44 | 0.25 | 50.4 | 2.4 | 4.8 |
| $1 \times 10^{-4}$ | 20.7 | 0.26 | 1.3 | 11.6 | 0.3 | 47.0 | 1.5 | 3.2 |
| $5 \times 10^{-4}$ | 3.96 | 0.19 | 4.8 | 48.3 | 1.7 | 37.5 | 2.2 | 5.9 |
| $1 \times 10^{-3}$ | 1.57 | 0.04 | 2.6 | 92.5 | 3.1 | 28.4 | 1.2 | 4.2 |
| $5 \times 10^{-3}$ | 0.153 | 0.005 | 3.2 | 414 | 15 | 12.4 | 0.5 | 4.0 |
| | | Mean | 3.9 | | | | Mean | 5.1 |

In Table II the same is given for methanol and methanolic solutions of KCl. The values are in relatively good agreement with the data from literature[7].

The indicated standard errors in the computed $\zeta$-potential were obtained in the same manner as described in the previous paper[12]. It must be emphasised that no claim is made that some »real« value of the $\zeta$-potential lies within the tabulated limits of the standard error, but that the technique itself is subject to this limit of accuracy yielding the mentioned values. The mean of the standard errors of about 7% (aqueous solutions) indicates that this method of measuring $\zeta$-potentials is only slightly less accurate than the streaming potential method. This statement can apply only to material in which no changes by electrolysis are possible. In the case of conducting material (e. g. silver halides) special care must be taken to avoid changes in the composition of the material of the plug or changes in the surface of the particles.

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## IZVOD

### Elektrokinetičke studije u disperznim sistemima. II. Elektroosmotski aparat

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Opisan je aparat za mjerenje elektroosmotskog transporta. Tok struje mogao je biti ograničen na svega nekoliko mikroampera zahvaljujući vrlo finoj kapilari, kojom se mjeri tok tekućine. Porozni čep od materijala, koji se ispituje, formira se u dvostrukoj koaksijalnoj epruveti centrifugiranjem. Statističkom analizom rezultata mjerenja elektroosmotskog volumnog transporta na česticama kvarca u vodenim i metanolnim otopinama KCl ustanovljena je standardna pogreška $\zeta$-potencijala od 7%.

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