

# ELECTROKINETIC POTENTIALS. X. THE EFFECT OF PARTICLE SIZE ON THE POTENTIAL\*

BY HENRY B. BULL AND ROSS AIKEN GORTNER

## Introduction

The present study was an outgrowth of an effort to obtain a standard material for the investigation of electrokinetic phenomena. Much of the work on electrokinetics has been done on ill-defined materials and it has been almost impossible for other workers to repeat each other's results with any degree of precision. It seemed desirable that the different methods for determining the electrokinetic potentials be checked against each other using the same standard material. Accordingly it was decided to use very pure quartz powder for this purpose. Investigation however showed that the situation was not simple because the electrokinetic potential on quartz particles depends upon particle size. Accordingly it was necessary to study the effect of particle size on the potential.

Mooney<sup>1</sup> reports a decrease in cataphoretic mobility of red oil, benzyl chloride, iodobenzene, tribromhydride and dimethylaniline measured in distilled water as the particle size is decreased. He found the mobility to start decreasing with the decreasing particle size at about  $150\mu$ .

Abramson's and L. Michaelis'<sup>2</sup> work on the cataphoresis of protein-covered particles seems to indicate that with such particles the mobility is independent of the size.

## Experimental

Five pounds of pure well-formed quartz crystals were ground† to pass a twenty-mesh sieve, digested with aqua regia for six hours, washed by decantation forty times with distilled water and ten times with conductivity water, sucked dry on a Büchner funnel, and then heated at  $800^{\circ}\text{C}$ . for 12 hours in a muffle furnace. This quartz was subsequently separated into nine portions by means of different mesh screens.

The only electrolyte solutions used in this investigation were  $1.0 \times 10^{-4}\text{ N}$  and  $2.0 \times 10^{-4}\text{ N NaCl}$ . The NaCl was the purest obtainable. It was dried at  $400^{\circ}$  before weighing for solution. The water used in making the solution was twice distilled and had a conductance of about  $1.5 \times 10^{-5}$  mhos. The volumetric apparatus was calibrated. The solutions were used the same day they were made.

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<sup>1</sup> J. Phys. Chem., **35**, 331 (1931); Phys. Rev., (2) **23**, 396 (1924).

<sup>2</sup> J. Gen. Physiol., **12**, 587 (1929).

† Thanks are due Dr. C. C. Furnas of the Experimental Station, U. S. Bureau of Mines for grinding this quartz.

The streaming potential method was used for determining the electrokinetic potential on the quartz. The apparatus was the same as that described by Bull and Gortner.<sup>3</sup> No constant temperature bath was employed but all the work was done in a room the temperature of which was  $24.5 \pm 0.5^\circ$ .

The conductivity of the salt solution in contact with  $4.6\mu$  size quartz was determined in the streaming potential cell. The other conductivities reported are those of the solution in bulk. This is deemed permissible because it was found that the surface conductance of the quartz larger than  $4.6\mu$  was small enough so that surface conductance could be neglected. The bulk conductivi-

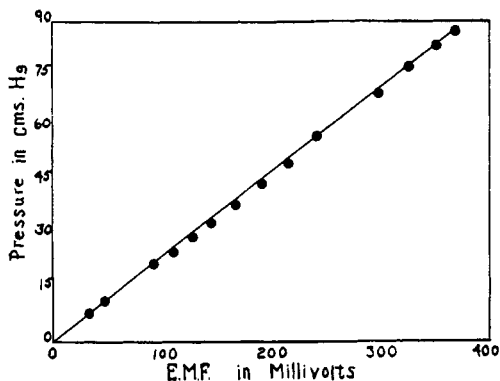


FIG. 1

Showing the relation between the streaming potential and the pressure, as experimentally determined in our apparatus using a cellulose diaphragm and  $1.0 \times 10^{-4}$  N NaCl, as the liquid was being streamed thru the diaphragm

ties were determined using a conductivity cell described in detail by Washburn<sup>4</sup> for specific conductances in the range between  $10^{-6}$  and  $10^{-4}$  mhos. The resistance was determined with a Leeds and Northrup alternating current galvanometer. The cell constant was determined with both N/10 and N/100 KCl using the Kohlrausch values. Head phones tuned to 1000 cycles vibrations were used to determine the cell constant.

Since it was our original intention to obtain a standard material for electrokinetic work, and to check the streaming potential method against cataphoretic methods, using this material, we ground some of our quartz in an agate mortar until it remained in suspension when mixed with water. This quartz was packed in a diaphragm and its  $\zeta$ -potential determined. The theory demands that there exist a linear relationship between the pressure applied on the liquid streaming thru the diaphragm and the electrical potential observed across the diaphragm as is shown in Fig. 1 for cellulose and an aqueous solution of  $1.0 \times 10^{-4}$  N NaCl.

<sup>3</sup> J. Phys. Chem., **35**, 309 (1931).

<sup>4</sup> J. Am. Chem. Soc., **38**, 2431 (1916).

To our surprise we found no such relationship with our quartz but instead, as is shown in Table I and Fig. 2, where the pressure is the abscissa and the streaming potential is the ordinate, we found a decreasing slope as we increased the pressure.

We found the same behavior to hold with  $2.0 \times 10^{-4}$  N NaCl and in later work used this concentration. Much time was spent in trying to determine the cause of this deviation from a straight line.

It is one of the fundamental requirements in the derivation of the streaming potential equation for calculating the zeta potential that Poiseuille's law for the flow of liquids thru capillaries be obeyed. It occurred to us that our difficulty might lie in the failure of this law of flow at higher pressures. This law states that the volume of liquid passing any cross section of a capillary in unit time is

$$V = \frac{\pi r^4}{8\eta} \frac{P_1 - P_2}{l}$$

where

$\eta$  = coefficient of viscosity of the liquid flowing

$r$  = radius of capillary

$P_1 - P_2$  = difference in pressure between the two ends of the capillary

$l$  = length of capillary.

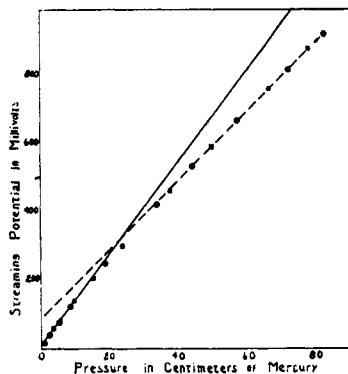


FIG. 2

Showing relation between pressure and the streaming potential with a heterogeneous mixture of quartz particles (sizes between  $.5\mu$  and  $36\mu$ ) and  $1.0 \times 10^{-4}$  N NaCl

TABLE I

Showing the Relationship between the Streaming Potential and Hydrostatic Pressure for a Quartz Diaphragm through which a  $1.0 \times 10^{-4}$  N Solution of NaCl was being streamed, the Quartz Particles being Non-uniform in Size.

Pressure (P) cm. Hg	Streaming Potential (H) mv.	H/P	Pressure (P) cm. Hg	Streaming Potential (H) mv.	H/P
With decreasing pressure					
1.0	19.5	19.50	77.5	885.0	11.42
2.4	40.5	16.88	66.1	767.5	11.61
5.1	77.5	15.20	49.7	593.0	11.93
8.7	124.0	14.25	37.2	463.0	12.45
18.8	251.0	13.35	23.5	304.0	12.94
33.7	423.0	12.55	15.1	208.0	13.78
43.9	536.0	12.21	9.7	141.5	14.59
57.0	670.5	11.76	5.5	86.5	15.73
71.7	821.0	11.45	3.5	61.5	17.57
82.1	928.0	11.30	1.2	25.5	21.25

One test of this law is to determine the relation between the rate of flow of a liquid thru a capillary as a function of the pressure applied. Poiseuille's law demands that this function be linear and that the volume of the liquid in unit time per unit pressure be a constant. Accordingly the rate of flow thru a quartz diaphragm at different pressures was studied. The quartz diaphragm used was prepared from the same sample of quartz as that employed to obtain the data for Table I. The results shown in Table II were obtained. The data in Table II show that there is not a sufficient deviation from Poiseuille's law to explain the lack of linearity between the pressure and the streaming potential.

TABLE II

Testing Poiseuille's Law of Flow thru a Quartz Diaphragm made of a Heterogeneous Mixture of Quartz Particles (sizes between  $.5\mu$  and  $36\mu$  in diameter) with an Aqueous Solution of  $2.0 \times 10^{-4}$  N NaCl.

Pressure (P) cm. Hg	Rate of Flow (V) grams of solution per min	V/P	Pressure (P) cm. Hg	Rate of Flow (V) grams of solution per min	V/P
8.0	.350	.0437	58.4	2.709	.0464
17.2	.786	.0457	67.0	3.126	.0466
26.3	1.190	.0452	75.9	3.462	.0456
37.4	1.750	.0468	82.3	3.950	.0480
48.0	2.260	.0461			

It was then decided to investigate the effect of particle size on the streaming potential. To this end that portion of the quartz powder which passed a 20 mesh sieve was further separated by sieving into nine portions. The particle size was assumed to be the arithmetic mean between the sieve size it was passed thru and that upon which it was retained. The three smallest sizes, i.e.,  $4.59\mu$ ,  $31.1\mu$ , and  $74.91\mu$  were determined by measurement of a number (75-100) of particles with a calibrated microscope and then taking the average of these measurements.

The  $4.59\mu$  size was packed in a diaphragm 1.1 cm. long and 2 cm. in diameter. The larger sized samples were packed in diaphragms 9.5 cm. long and 2 cm. in diameter. With this arrangement a convenient rate of liquid flow was obtained. Perforated gold electrodes were used at each end of the diaphragm. With the smaller quartz ( $98\mu$  and below) a thin layer (about 1 mm.) of  $214\mu$  quartz was placed at each end of the diaphragm to keep the smaller quartz from washing thru the perforations in the electrodes. The diaphragms were washed with at least 500 cc. of the solution and were then allowed to remain 12 hours in contact with a portion of the electrolyte solution to be used. This portion was replaced by fresh solution before a measurement was attempted. The values reported and used in the graph of the results are the average of at least six or more readings.

## Results

The results of the electrokinetic studies on the nine different particle sizes of the quartz are given in Table III thru Table XI, summarized in Table XII and graphed in Fig. 3.

TABLE III

 $2 \times 10^{-4}$  N NaCl and  $630\mu$  Quartz

Pressure cm. in Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. Hg (P)	Streaming Potential in millivolts (H)	H/P
2.03	61.0	30.06	0.98	28.0	28.56
0.23	7.0	30.74	0.57	18.0	31.82
1.76	50.0	28.42	1.06	33.0	31.14
2.70	80.0	29.65	0.78	20.0	25.27
3.49	90.0	25.70	Average H/P = 29.04		

TABLE IV

 $2 \times 10^{-4}$  N NaCl and  $330\mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
0.71	20.0	28.29	1.23	35.0	28.42
1.33	40.0	30.06	0.90	25.0	27.61
.80	25.0	31.14	Average H/P = 29.10		

TABLE V

 $2 \times 10^{-4}$  N NaCl and  $214\mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
2.57	80.0	31.01	2.90	90.0	31.01
2.54	75.0	29.51	2.36	70.0	29.65
2.71	80.0	29.51	3.27	100.0	30.46
3.01	90.0	29.92	Average H/P = 30.15		

TABLE VI

 $2 \times 10^{-4}$  N NaCl and  $163\mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
2.93	90	30.76	3.31	100	30.23
3.08	90	29.21	2.81	80	28.49
3.28	95	28.97	2.84	80	28.19
Average H/P = 29.31					

TABLE VII

 $2 \times 10^{-4}$  NaCl and  $128\mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
1.11	31.0	27.92	1.29	34.0	26.36
2.72	74.0	27.21	3.57	99.0	27.73
4.61	128.0	27.77	9.9	254.0	25.66
11.4	293.0	25.70	17.6	453.0	25.74
20.9	544.0	26.03	22.9	598.0	26.11

Average H/P = 26.62

TABLE VIII

 $2 \times 10^{-4}$  N NaCl and  $98\mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
3.86	104.0	26.94	19.5	465.0	23.85
9.1	223.0	24.51	34.2	830.0	24.27
21.9	545.0	24.89	1.61	38.0	23.60
31.4	775.0	24.68	3.57	84.0	23.53
1.53	40.0	26.14	8.6	188.0	21.86
4.08	103.0	25.25	18.7	423.0	22.62
10.6	250.0	23.58	34.0	780.0	22.94

Average H/P = 24.19

TABLE IX

 $2 \times 10^{-4}$  N NaCl and  $74.9\mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
1.90	40.0	21.05	4.06	97.0	23.89
3.97	89.0	22.42	9.60	216.0	22.50
9.60	210.0	21.88	19.50	453.0	23.23
18.70	431.0	23.05	27.60	635.0	23.01
28.40	665.0	23.42	37.30	850.0	22.79
1.42	35.5	25.00			

Average H/P = 22.93

TABLE X

 $2 \times 10^{-4}$  N NaCl and  $31.1 \mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
1.41	30.0	21.28	29.70	595.0	20.03
3.75	78.0	20.80	40.30	818.0	20.30
9.20	177.0	19.24	52.50	1097.0	20.90
19.80	392.0	19.80	52.10	1099.0	21.09
29.80	604.0	20.27	4.50	85.0	18.89
40.40	826.0	20.45	9.00	166.5	18.50
51.10	1057.0	20.68	20.10	388.0	19.30
62.80	1310.0	20.86	29.00	567.0	19.55
1.33	30.0	22.56	40.10	792.0	19.75
3.77	77.0	20.42	50.60	1006.0	19.88
9.60	181.0	18.85	59.80	1191.0	19.92
19.60	381.0	19.44	Average H/P = 20.12		

TABLE XI

 $2 \times 10^{-4}$  N NaCl and  $4.59 \mu$  Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
3.47	23.0	6.63	47.20	302.5	6.41
11.60	65.0	5.60	62.50	392.0	6.27
18.40	116.0	6.30	73.50	456.0	6.20
31.40	199.0	6.34	Average H/P = 6.25		

TABLE XII

Summary of Electrokinetic Potentials at a Quartz-Aqueous  $2.0 \times 10^{-4}$  N NaCl Interface. Showing the Effect of Particle Size.

Particle diameter in $\mu$	$\log \mu$	H/P	$\kappa_a \times 10^6$ mhos	$H\kappa_a/P$	$\log H\kappa_a/P$
630	2.799	29.04	28.90	83.93	1.924
330	2.519	29.10	28.90	84.10	1.925
214	2.330	30.15	28.90	87.13	1.940
163	2.212	29.31	28.90	84.71	1.928
128	2.107	26.62	28.90	76.93	1.886
98	1.991	24.19	28.90	69.91	1.845
74.9	1.875	22.93	28.90	66.27	1.821
31.1	1.493	20.12	28.90	58.15	1.765
4.59	0.662	6.25	35.81	22.38	1.350

### Discussion

It is our belief that the deviation from a linear relation between pressure and the streaming potential is due to the fact that the  $\zeta$ -potential on the quartz particles is different for different size particles. This lack of linearity was observed only with a heterogeneous mixture of particle sizes. When the quartz was separated into its fractions of relatively uniform particle size a

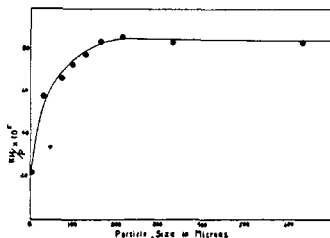


FIG. 3  
Showing the relation between the electrokinetic potentials at a quartz-aqueous  $2.0 \times 10^{-4}$  N NaCl interface for different particle sizes

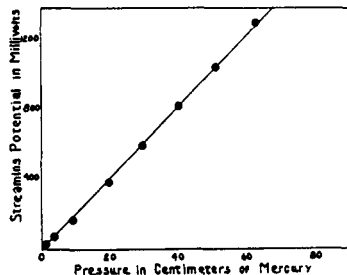


FIG. 4  
Showing relation between pressure and electrokinetic potential for a homogeneous particle size. (Data from Table X.  $2 \times 10^{-4}$  N NaCl and  $31.1\mu$  quartz).

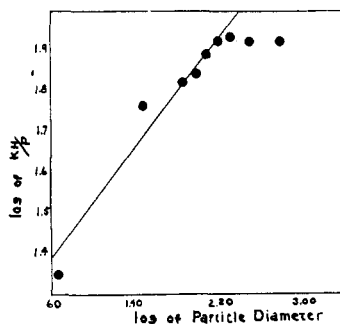


FIG. 5  
Plot of  $\log H_K/P$  against  $\log \mu$ . The straight line is drawn on the assumption that  $H_K/P$  varies as the cube root of  $\mu$

good straight line was obtained between pressure and the streaming potential as is demonstrated in Fig. 4 plotted from the data of Table X.

It seems probable that as the pressure is increased the smaller quartz particles are displaced into the places of maximum flow, thus protecting the larger particles and diminishing their importance in the picture, and, since it is the larger particles which have the higher potential, naturally the ratio between the streaming potential and pressure decreases, thus producing the effect shown in Fig. 2.

In Fig. 5 the log of the particle diameter is plotted as the abscissa against  $\log H_K/P$  as the ordinate.

From a particle size of  $4.59\mu$  to  $214\mu$  an approximate straight line is obtained whose slope is  $1/3$ , which means that  $H_K/P$  varies roughly as the cube root of the diameter of the particle. It is suggestive that as we decrease the particle size the ratio of edge length and number of corners to the surface area of the particles increases. Now there is reason to believe that, due to un-



satisfied valencies in the crystal lattice, more adsorption occurs at the edges and corners than on the flat surfaces<sup>5</sup> so that as we decrease the particle size of the quartz we should expect more adsorption per unit area, which would be equivalent to having a higher salt concentration at the interface which, in turn, would undoubtedly produce a lower electrokinetic potential and thus account for the fact that the smaller quartz particles were found to have a smaller electrokinetic potential.

### Summary

1) Pure quartz crystals were ground to pass a 20 mesh sieve, thoroughly cleaned and separated into nine portions according to the particle size. Electrokinetic studies were conducted on this quartz in an aqueous solution of  $0.20 \times 10^{-3}$  N NaCl.

2) In a heterogeneous mixture of different size quartz particles, no linear relation was found between the pressure forcing the liquid thru the quartz diaphragm and the streaming potential. Poiseuille's law was found to hold with this quartz.

3) In a more homogeneous mixture of quartz particles a good linear relation was found between the pressure forcing the liquid thru the quartz diaphragm and the streaming potential.

4) Between a particle size of  $4.59\mu$  and  $214\mu$  the surface potential was found to increase roughly as the cube root of the diameter.

5) It is suggested that the lack of linearity between the streaming potential and the pressure in a heterogeneous mixture of particle sizes is due to the fact that the smaller particles have a smaller surface potential.

6) It is also suggested that the smaller particles have a smaller surface potential because they adsorb a greater amount of salt per unit area.

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<sup>5</sup> Taylor: J. Phys. Chem., 30, 145, (1926).