440. *Sedimentation Potentials. Part II.*[1] *The Determination of the Zeta Potentials of Some Solid Surfaces in Aqueous Media, by Use of Sedimentation Potential Measurements.*

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Measurements have been made of the sedimentation potentials set up by five different solids (Pyrex glass, fused silica, silicon, fused alumina, and carborundum) in potassium chloride and barium chloride solutions over the concentration range 1—7 × 10^{-5}N. The results obtained have been used to calculate the values of the zeta potentials of the surfaces by using a modified form of the Smoluchowski electrokinetic equation. Except in the case of carborundum, fair agreement has been found between zeta potentials calculated from sedimentation potential data, and figures obtained by workers using streaming potential and other more familiar techniques. The discrepancies in the results obtained from carborundum are thought to be due to the presence of varying amounts of carbon impurity.

PART I [1] of this study of sedimentation potentials was concerned principally with the development of a suitable experimental technique and its subsequent application to confirm the validity of using a modified form of the familiar Smoluchowski electrokinetic equation [2] to calculate values of zeta potentials from sedimentation potential data. The experimental work has now been extended to investigate the sedimentation potentials set up by a variety of solid surfaces in both potassium and barium chloride solutions. The present paper deals with the results of these investigations and includes a comparison between the values of zeta potentials calculated from sedimentation data and figures obtained on similar surfaces by other workers. Improvements in experimental technique have resulted in an increase in the accuracy of the calculated zeta potentials, and in the light of these improvements revised figures are given for the soft glass and Pyrex glass surfaces used in Part I.[1]

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[1] Part I, Elton and Peace, *J.*, 1956, 22.

[2] " Handbuch der Elektrizität und des Magnetismus," Graetz, Liepzig, 1921, Vol. II, p. 385.

EXPERIMENTAL

Materials.—Solid materials were ground and sieved to a close size range to ensure as far as possible uniform particle radius. The dry sieved solid was washed with successive changes of benzene followed by a similar treatment with sulphuric acid. This was followed by rinsing with tap water, distilled water, and finally equilibrium conductivity water, in which the material was left immersed overnight before being dried at 110°. The mean Martin's radius [3] was determined microscopically for each sample.

(a) *Fused silica.* This was supplied by the Thermal Syndicate Ltd. in large fragments which were ground and sieved to a mean Martin's radius of 278 μ.

(b) *Silicon.* Spectroscopically pure silicon, supplied privately, was sieved to a mean Martin's radius of 106 μ.

(c) *Pyrex glass.* This was ground and sieved to a mean Martin's radius of 297 μ.

(d) *Carborundum.* The Morgan Crucible Co. kindly supplied a specimen of pure carborundum. This was sieved to obtain a sample having a mean Martin's radius of 123 μ.

(e) *Fused alumina.* A sample of pure fused alumina having a mean Martin's radius of 114 μ was obtained by sieving powder supplied by the Thermal Syndicate Ltd.

The water used throughout was equilibrium conductivity water of specific conductivity $0{\cdot}8$—$1{\cdot}0 \times 10^{-6}$ ohm^{-1}, prepared by an ion-exchange process.

The two electrolytes, potassium chloride and barium chloride, were prepared by recrystallising the "AnalaR" salt several times from equilibrium conductivity water, heating it to dryness in a platinum dish, and storing it in a vacuum desiccator.

Apparatus and Technique.—The sedimentation cell was similar to that designed by Quist and Washburn; [4] silver–silver chloride electrodes were used. A specially constructed valve millivoltmeter was used to measure the potentials developed, an overall sensitivity of 0·02 mv being obtained. Conductivities were determined on a conventional A.C. Wheatstone bridge, all experiments being carried out at room temperature, namely, 21° ± 5°. Further details are given by Peace.[5]

RESULTS and DISCUSSION

It was shown in Part I that equation (1), obtained by modification of Smoluchowski's electrokinetic equation, normally applied to streaming potential measurements, can be used to obtain values of zeta potential from sedimentation data:

$$E = \frac{MHg\,(\rho_2 - \rho_1)\zeta\varepsilon}{4\pi\eta\kappa\rho_2\,1000} \times \frac{1}{9 \times 10^{11}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E = sedimentation potential (v), M = total weight of solid per unit volume of suspension between the electrodes (g.), κ = specific conductivity of the solution (ohm^{-1}), H = distance between the electrodes (cm.), ζ = zeta potential (mv), η = viscosity of solution (poise), ρ_2 = density of solid, ρ_1 = density of liquid, ε = dielectric constant of liquid.

This equation has been used to calculate the zeta potentials of the various solid surfaces discussed below from the corresponding sedimentation potential figures, the method used being similar to that employed in Part I for soft glass and Pyrex glass, *i.e.*, using a graph of E/M against $1/\kappa\eta$ (see below). When Part I was written it did not appear that the sedimentation potential was sufficiently temperature-dependent to warrant any form of correction for the variation in room temperature between successive experiments. However, with subsequent improvements in apparatus and technique it has been found possible to increase significantly the accuracy of the calculated zeta potential figures by careful correction of the temperature-dependent variables contained in equation (1), principally κ, M, and η. The temperature dependence of M arises from the fact that it is

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[3] Cadle, "Particle Size Determination," Interscience, London, 1955, p. 135.

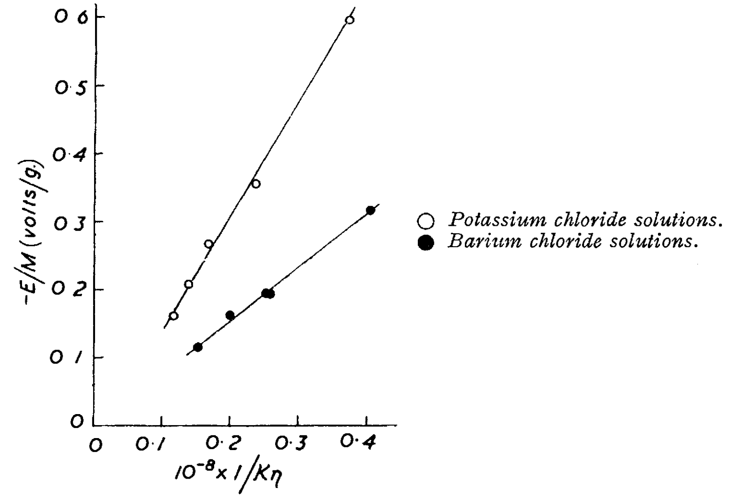
[4] Quist and Washburn, *J. Amer. Chem. Soc.*, 1940, **62**, 3169.

[5] Peace, Ph.D. Thesis, London, 1956.

related to the velocity of fall of the particles, which is in turn dependent on the temperature of the aqueous medium. However, since the sedimentation velocities of the particles used were outside the range of Stokes's law it was not possible to apply the normal temperature correction, and consequently use was made of two flow equations [6] designed to cover the range of velocities encountered in these experiments.

A more accurate figure of —76·5 mv, based on the above temperature corrections, for the zeta potential at 25° of the soft glass spheres in 10^{-5}N-potassium chloride solution is in fair agreement with the results of Eversole and Boardman,[7] who obtained a figure of —87·3 mv from streaming potential measurements on soft glass capillaries in similar solutions.

It was noted in the earlier work on soft glass that the graphs obtained by plotting E/M against $1/\kappa\eta$ were linear over the concentration range studied, namely, 1—7 × 10^{-5}N-potassium chloride, indicating a constant zeta potential in this range. This linear relation has been found to hold within the same concentration limits for all the solids so far investigated, in both potassium chloride and barium chloride solutions. A typical set of results, given by fused silica, is shown in the Figure.



This effect is almost certainly due to the use of silver–silver chloride electrodes for recording the sedimentation potentials, since it has been shown by Dulin and Elton [8] that at low concentrations of potassium chloride the effect of the silver chloride is to raise the numerical value of the surface charge and lower that of the zeta potential of fused silica. Thus the change in zeta potential over the experimental concentration range might well be within the total error of the method as a whole, estimated at not more than ±5%.

It is unfortunately not possible to extend the concentration range outside the limits given above, since in extremely dilute solutions, *i.e.*, less than 1 × 10^{-5}N, difficulties arise owing to the high internal resistance of the cell and to electrode instability, whereas above 7 × 10^{-5}N, the potentials become too small to measure accurately.

Fused Silica.—The variation in E/M with $1/\kappa\eta$ for fused silica in both potassium chloride and barium chloride solutions is illustrated in the Figure. Tables 1 and 2 show a comparison between the values of zeta potential calculated from the above data using equation (1) and values obtained by other workers using streaming potential and sedimentation velocity methods.

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[6] Davies, *Proc. Phys. Soc.*, 1945, **57**, 259.
[7] Eversole and Boardman, *J. Phys. Chem.*, 1942, **46**, 914.
[8] Dulin and Elton, *J.*, 1952, 286.

TABLE 1. *Fused silica in potassium chloride solutions.**

Concn. of KCl (N)	ζ_1	ζ_2	ζ_3	ζ_4	ζ_5
1×10^{-4}	—	−129	−129	−134	−73·5
5×10^{-5}	−109	−136	−135	—	—
1×10^{-5}	−109	−156	−146	−142	−86

* Here and throughout values of ζ are in mv.

ζ_1, Values from the present work. ζ_2, Values from sedimentation velocity measurements by Dulin and Elton.[8] ζ_3, Values from a system similar to that of ζ_2 but saturated with respect to silver chloride.[8] ζ_4, Values from streaming potential measurements with vitreous silica capillaries by Jones and Wood [9] using silver–silver chloride electrodes. ζ_5, Values from streaming potential measurements on quartz capillaries by Eversole and Boardman.[7]

The change in ζ_3 and ζ_4 over the range 5×10^{-5} to 1×10^{-5}N is less than ±5%, and hence might well pass unnoticed in sedimentation potential measurements.

Results from similar systems in dilute barium chloride solutions are shown in Table 2.

TABLE 2. *Fused silica in barium chloride solutions.*

Concn. of $BaCl_2$ (N)	ζ_1	ζ_2	ζ_3
1×10^{-4}	—	−59·5	−73
5×10^{-5}	−50	−61	—
1×10^{-5}	−50	−74	−93

ζ_1, Values from the present work. ζ_2, Values from sedimentation velocity measurements by Dulin and Elton.[10] ζ_3, Values from streaming potential measurements with vitreous silica capillaries by Wood and Robinson.[11]

Silicon.—A study of the zeta potentials of spectroscopically pure silicon calculated from sedimentation potential data shows a close similarity with the figures obtained for fused silica. Table 3 shows a comparison of the experimental results for the two materials.

These results indicate that both materials form similar surface layers when in contact with electrolyte solutions, and suggest that the silicon atom may possibly be the important factor in determining the magnitude of the surface charge and the associated zeta potential. This may be due either to reaction with water molecules to form a layer of silicic acid, which subsequently ionises,[12] or to the fact that the major part of the adsorption occurs only on the sites of the silicon atoms.

TABLE 3. *Comparison of results for fused silica and silicon.*

	Concn. range	Zeta potential (mv)			Concn. range	Zeta potential (mv)	
Electrolyte	(N)	Si	SiO_2	Electrolyte	(N)	Si	SiO_2
KCl	$1 - 5 \times 10^{-5}$	−99	−109	$BaCl_2$	$1 - 5 \times 10^{-5}$	−52	−50

Pyrex Glass.—The data obtained for Pyrex glass (ζ_1) are shown in Table 4, together with electrokinetic potentials (ζ_2) calculated by Ghosh, Choudhury, and De [13] from the results of Wigja [14] who used streaming potential methods on various Pyrex diaphragms

TABLE 4. *Pyrex glass.*

Specific conductivity (gemmhos)	ζ_1 (KCl)	ζ_1 ($BaCl_2$)	ζ_2 (KNO_3)	ζ_3 (KNO_3)
1·10	—	—	−132	−133
1·77	—	—	−130	−130
3·05	−94·5	−81	−125	−125·5
6·90	−94·5	−81	−107	−119
13·25	—	—	−109	−115·5

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[9] Jones and Wood, *J. Chem. Physics*, 1945, **13**, 106.
[10] Dulin and Elton, *J.*, 1953, 1168.
[11] Wood and Robinson, *J. Chem. Physics*, 1945, **14**, 251.
[12] O'Connor and Buchanan, *Trans. Faraday Soc.*, 1956, **52**, 397.
[13] Ghosh, Choudhury, and De, *Trans. Faraday Soc.*, 1954, **50**, 955.
[14] Wigja, Thesis, Utrecht, 1946.

of uniform particle radius in dilute potassium nitrate solutions. ζ_3 represents figures obtained by Wigja[14] from Pyrex capillary tubes, again by streaming potential measurements.

Carborundum.—The zeta potential (ζ_1) at the surface of a pure specimen of carborundum used in the present work is shown in Table 5 compared with values obtained by using sedimentation velocity methods on samples of the commercial material[15] (ζ_2).

TABLE 5. *Carborundum.*

Electrolyte	Concn. (N)	ζ_1	ζ_2	Electrolyte	Concn. (N)	ζ_1	ζ_2
KCl	1×10^{-4}	—	−102	$BaCl_2$	5×10^{-5}	−20·5	—
KCl	5×10^{-5}	−21	−109	$BaCl_2$	1×10^{-5}	−20·5	—
KCl	1×10^{-5}	−21	−122				

The marked difference between these two sets of values is not surprising in view of the high proportion of carbon impurity present in commercial carborundum, which in addition to modifying the surface may cause a considerable decrease in the specific resistance of the solid.

Fused Alumina.—It has been shown[16] that the zeta potential of aluminium oxide, as determined by streaming potential measurements, can vary between +70 and —59 mv depending on the initial pretreatment of the surface, *i.e.*, variation in the time and temperature of ignition, etc. Nevertheless, there is agreement between the value of the zeta potential of freshly ground aluminium oxide in water given by the above workers (approximately +40 mv) and the value of +40 mv obtained with dilute potassium chloride solutions and fused alumina in the present studies. In barium chloride solutions, the sedimentation potential method indicated a zeta potential of +42 mv.

As a result of the above comparisons between values of zeta potential obtained from sedimentation data and the figures given by other methods, it would appear that sedimentation potential techniques can be applied successfully, within certain concentration limits, to the determination of the electrokinetic potentials of solid surfaces. It is very probable that such discrepancies as do exist between zeta potential values obtained by different workers are due, not so much to differences in the theoretical treatments applied to the various experimental methods, as to the fact that they arise from the difficulty in obtaining reproducible surfaces on which to carry out comparative measurements. This has been clearly shown by O'Connor and Buchanan,[12] who measured streaming potentials across a bed of sieved quartz particles after initial treatment of the material with various electrolytes, followed by washing in conductivity water of specific conductivity 1 gemmho. The resulting values of ζ in conductivity water were consistent for a given pretreatment, but varied between —100 and —56 mv with different methods of pretreatment. As mentioned earlier, the same workers obtained an even greater range of zeta potentials from measurements on aluminium oxide, and Jones and Wood[9] have reported similar surface effects with streaming potential measurements in vitreous silica capillaries.

These considerations indicate clearly the necessity for stating the methods of preparation and cleaning of surfaces when reporting electrokinetic results. This would permit precise repetition of experimental determinations by future workers, and enable accurate comparisons to be made between the results of standard techniques, and the values from new methods for the determination of zeta potentials, by ensuring that similar solid surfaces are used in all cases.

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[15] Elton and Mitchell, *J.*, 1953, 3690.

[16] O'Connor, Johansen, and Buchanan, *Trans. Faraday Soc.*, 1956, **52**, 229.