5. *Sedimentation Potentials. Part I. The Measurement of Sedimentation Potentials in Some Aqueous and Non-aqueous Media.*

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An experimental study has been made of sedimentation potentials of glass particles in water and dilute aqueous potassium chloride, and of silica and glass particles in toluene and ether. The results for aqueous media have been used in a preliminary test of the theoretical equations of Smoluchowski and of Hermans. The potentials obtained in non-aqueous media appear to be electrostatic in origin, and cannot be interpreted on the basis of these electrokinetic equations.

ALTHOUGH sedimentation potentials were first investigated by Dorn (*Ann. Physik*, 1878, **3**, 20; *Wied. Ann.*, 1880, **10**, 46) over seventy years ago, the present state of knowledge concerning them is rather unsatisfactory. Theoretical considerations have been given by Smoluchowski (in Graetz's " Handbuch der Elektrizität und des Magnetismus," Leipzig, 1921, Vol. II, p. 385), by Hermans (*Phil. Mag.*, 1938, **26**, 650), and, more recently, by Booth (*J. Chem. Phys.*, 1954, **22**, 1956), but, as Booth points out, there are hardly any experimental results available with which to test the equations derived. The two most important experimental papers are those of Stock (*Anz. Akad. Wiss. Krakau*, **1913**, *A*, 131; 1914, *A*, 95), who studied potentials set up by quartz particles sedimenting in toluene and in ether, and of Quist and Washburn (*J. Amer. Chem. Soc.*, 1940, **62**, 3169), who used Pyrex glass particles in water and in dilute aqueous solutions. The present paper describes work which confirms and extends the results of Quist and Washburn and may be used in a preliminary test of the theoretical equations given by Smoluchowski, Hermans, and Booth (*locc. cit.*). Stock's results for toluene and ether have been partially confirmed.

EXPERIMENTAL

Materials.—Ground Pyrex glass, sieved to the size range 95 ± 10 μ, and cleaned as described by Elton and Hirschler (*J.*, 1952, 2953), was used to check the results of Quist and Washburn. Soft glass spheres, supplied by The English Glass Company, Ltd., were used in studies of the effect of particle radius on the sedimentation potential. Four batches of spheres, sieved to fairly uniform sizes (±7%), were used, the mean radii of the batches, determined microscopically, being (i) 51, (ii) 112, (iii) 216, and (iv) 372 μ. For the experiments with toluene and ether, ground fused silica, sieved to the size range 20 ± 2 μ and cleaned as described by Dulin and Elton (*J.*, 1952, 286), was used.

The water used throughout these experiments was equilibrium conductivity water, prepared by an ion-exchange process, and was of specific conductivity 0·8—1·0 × 10^{-6} ohm^{-1}. "AnalaR" potassium chloride was recrystallised several times from conductivity water. Ether was dried over calcium chloride and sodium, and redistilled; sulphur-free toluene was dried over potassium carbonate.

Apparatus and Technique.—Conductivities were determined on a conventional A. C. Wheatstone bridge.

The sedimentation cell used for the experiments with aqueous media was identical with that of Quist and Washburn (*loc. cit.*). Silver–silver chloride electrodes were prepared by Brown's method (*J. Amer. Chem. Soc.*, 1934, **56**, 646); the potentials were measured, earthed leads being used, on a valve millivoltmeter of standard design, being determined from measurements of the change in anode current; calibration of the instrument for various values of grid bias and circuit resistance was necessary. By suitably adjusting the grid bias of the valve it was possible to ensure that the current passing through the sedimentation cell during the taking of a measurement was less than 5 × 10^{-9} amp. Owing to the high internal resistance of the cell, readings were very sensitive to moisture in the air. The cell was therefore mounted inside an earthed metal box through which warm dry air was drawn during the experiment, and the voltmeter was housed in a dry, air-tight, earthed metal box, the controls being operated from outside. The 120-v battery supplying the high tension for the voltmeter was left on for several days before an experiment was started, in order to minimise voltage drift. With these precautions a sensitivity of 0·02 mv was obtained, the limiting factor generally being the stability of the electrodes.

The experimental technique was similar to that of Quist and Washburn (*loc. cit.*), except that the particles were previously equilibrated with the solution to be used by prolonged shaking. (This produced a rise in the specific conductivity of the solution.) The rate of flow of sedimenting particles could be adjusted by the operation of the tap leading from the reservoir of particles. A pointer moving over a scale was attached to the tap to facilitate the reproducing of flow rates, determined by the time taken for a known weight of powder to flow through the tap. The mass M per unit volume of suspension could then be calculated from the rate of flow and the velocity of sedimentation of the particles, determined in a separate experiment. The potential difference between any pair of the three electodes could be measured, and the steady value reached after the particles had been falling for a short time gave the sedimentation potential, after correction for any slight asymmetry potential present between the electrodes in the absence of falling particles.

The total potential difference measured in a given experiment was found to be directly proportional to the distance between the electrodes, indicating that the sedimentation field of the particles had become constant by the time that the top electrode had been reached. The measured potentials were found to be independent of the size of the silver–silver chloride electrodes used, agreement to within experimental error (±4%) being obtained with (*a*) wire electrodes of area 10^{-3} cm.^{2} or (*b*) plate electrodes of area 1 cm.^{2}. Other types of electrode tried, namely, of antimony and tungsten, proved unsatisfactory owing to lack of stability.

Suitable adjustment of the grid bias of the voltmeter made it possible to measure potentials in a given system while passing different currents. In all experiments it was found that the measured potentials were not affected, within experimental error, by varying the current passing between 2·5 × 10^{-9} and 3 × 10^{-8} amp.

The sedimentation cell used for the work on non-aqueous liquids was very similar to that used by Stock (*loc. cit.*). It consisted of a long Pyrex-glass tube of diameter 1·4 cm., fitted with a ground-glass joint at each end, and having two sealed-in platinum wire electrodes (each of area 5 × 10^{-4} cm.^{2}) 110 cm. apart. The potentials were measured with a quadrant electrometer, suitably connected, as described by Stock (*loc. cit.*). The silica powder was made to fall through the non-aqueous liquid simply by inverting the cell.

RESULTS AND DISCUSSION

(a) *Aqueous Media.*—The experiments were carried out at room temperature, namely 20° ± 6°, and it was found that the sedimentation potential gradient, E, for a given system was independent of temperature over this range. For purposes of comparison of different systems it was found convenient to plot E as a function of $\kappa\eta$ (where κ is the specific conductivity and η is the viscosity of the liquid), which is also practically independent of temperature.

The Pyrex powder used was of the same size range as that used by Quist and Washburn (*loc. cit.*). It was confirmed that the sedimentation potential was directly proportional to M, the direction of the potential gradient indicating that the Pyrex particles were negatively charged. The Table gives the ratio E/M obtained by us for water and two aqueous solutions of potassium chloride, of measured conductivity after equilibration with the glass. Quist and Washburn (*loc. cit.*) do not give the conductivities of their solutions of sodium chloride, but our results for E are in fairly good agreement with theirs at corresponding concentrations. Quist and Washburn calculated the electrokinetic potential ζ for water from their results for the non-spherical particles, assuming the applicability of Smoluchowski's equation (*loc. cit.*) for spherical particles. This equation is

$$E = \varepsilon\zeta g\,(\rho_2 - \rho_1)M/4\pi\,\kappa\,\eta\rho_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ε is the dielectric constant in the diffuse part of the electrical double layer; g is the gravitational constant; and ρ_2, ρ_1 are the densities of the solid and solution respectively.

Solution	$10^6\,\kappa$ * (ohm^{-1})	$10^2\,E/M$ (v/g.)	ζ_1 (v)	ζ_2 (v)	ζ_3 (v)	ζ_4 (v)	ζ_5 (v)
10^{-4}N-KCl	14·6	7·6	0·14	0·14 †	0·24	0·24	0·12
10^{-5}N-KCl	3·0	35	0·14	0·10	0·23	0·17	0·13
Water	1·1	133	0·19	0·12	0·33	0·20	0·13

* The specific conductivity of the water used by Quist and Washburn was $1{\cdot}4 \times 10^{-6}$ ohm^{-1}. The specific conductivities of the salt solutions were not given, so it has been assumed, for the purpose of approximate comparison, that these were the same as ours.

† This value is likely to be less accurate than the rest of Quist and Washburn's results, as the results of only a few determinations are quoted, and these are rather scattered.

This equation was also obtained by Booth (*loc. cit.*) for the limiting case where the double-layer thickness is much smaller than the size of the particles, and the mobilities of all the ions are approximately equal. Both of these conditions are fulfilled by our systems. The Table also gives the values of ζ calculated from our results (ζ_1) and from those of Quist and Washburn (ζ_2) (*loc. cit.*) by using equation (1), and corresponding values ζ_3, ζ_4, obtained by using Herman's equation (*loc. cit.*), *viz.* :

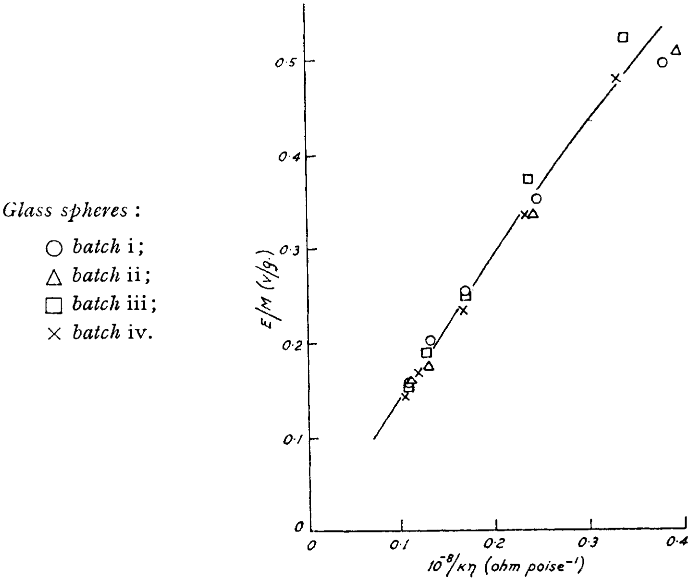
$$E = 7\varepsilon\zeta g\,(\rho_2 - \rho_1)\,M/48\pi\,\kappa\,\eta\rho_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation, differing from (1) by the factor 7/12, takes into account the effect of relaxation forces, set up by the distortion of the electrical double layer, on the sedimentation potential.

Finally the Table gives, for comparison, ζ_5, the electrokinetic potential of Pyrex glass in dilute potassium nitrate solutions, calculated by Ghosh, Choudhury, and De (*Trans. Faraday Soc.*, 1954, **50**, 955) from the results of Wijga (Thesis, Utrecht, 1946). It is seen that agreement is reasonable between our results and those of Quist and Washburn, it being borne in mind that it was necessary to assume values for the conductivity of their solutions. The values of ζ calculated from equation (1) agree better with ζ_5 (from streaming potentials) than do those calculated from equation (2). We may therefore make the following tentative deductions : (*a*) The assumption that equations (1) and (2) may be applied to non-spherical particles is apparently not greatly in error. (*b*) If the above-mentioned assumption is exactly valid, then equation (1) appears to be more nearly correct than equation (2). Further discussion of this point is given below (p. 25).

Quist and Washburn did not investigate the effect of change of particle size on the measured potentials. Equations (1) and (2) both demand that the E.M.F. should depend on the mass of particles per c.c. of suspension, but not on the particle size, so long as this is much greater than the double layer thickness. We have checked this, using soft glass spheres, of the four sizes mentioned above, in dilute aqueous potassium chloride. The glass was rather soluble in water, so in order to avoid the use of solutions of too high a conductivity, the spheres were leached many times with conductivity water before bringing them into contact with the solution to be used. In this way it was possible to ensure that no change in conductivity of the solution used occurred during the time necessary to carry out a run. The values of E/M for the four particle sizes are shown in the Figure as a function of $1/\kappa\eta$. Within experimental error all the points lie on a straight line of slope $0{\cdot}4_4 \times 10^9$ e.s.u. cm.^{2} sec.$^{-1}$, through the origin. We deduce, therefore, that E/M is independent of particle size. Furthermore, equations (1) and (2) both lead to the conclusion that ζ is approximately independent of ionic strength over the range considered ($\kappa = 3 \times 10^{-6}$ to 1×10^{-5} ohm^{-1}; $c \doteqdot 1$—7×10^{-5} N).

This is often observed for such extreme dilutions when silver–silver chloride electrodes are used [see, *e.g.*, Ghosh, Choudhury, and De (*loc. cit.*); Dulin and Elton (*loc. cit.*)].



Equation (1) gives $\zeta = 0{\cdot}08$ v, and equation (2) gives $\zeta = 0{\cdot}14$ v. As was the case for the Pyrex powder, equation (1) gives the more satisfactory value of ζ, which is usually found to be approx. 0·1 v for glass in very dilute aqueous solutions. We may take the results of these two sets of experiments as a preliminary indication that equation (1), due to Smoluchowski, is more satisfactory than equation (2), due to Hermans. Further tests are obviously necessary before final quantitative conclusions can be drawn. For these tests it will be desirable to experiment also with smaller particles than those used here, which show some deviation from Stokes's law, especially for the largest sizes. This effect does not, however, influence the agreement between the values of E/M found for the different particle sizes.

(b) *Non-aqueous Media.*—The results of the experiments with non-aqueous liquids were less satisfactory than of those with aqueous liquids. Despite careful precautions to purify and dry the liquids and to clean the silica particles, results were rather variable from day to day. The potentials, however, were of the same order as those obtained by Stock (*loc. cit.*), and the direction of E indicated the presence of a negative charge on the silica particles. A few runs were also done with soft glass spheres of radius 59 $\pm 5\,\mu$, with similar lack of reproducibility. This is very probably due to the very low conductivity of the liquids, which made the effect almost purely electrostatic. Marked agglomeration of the particles also occurred, especially in the toluene, resulting in turbulent settling. When the cloud of particles was around one of the electrodes, a deflection was obtained on the electrometer which did not depend on whether the other electrode was connected or not. When the cloud had passed the electrode there was an equally large deflection in the other direction, indicating that a positive ion atmosphere was situated behind the sedimenting particles. This counter deflection could not be due to an instrument effect as the same deflection was obtained if the electrode was not connected until immediately after the cloud of particles had passed it. Since the potential measured depended only on the number of particles around the electrode being used, and was independent of what was happening in the rest of the tube or near the other electrode, neither equation (1) nor equation (2) was applicable. It does not, therefore, appear profitable to investigate further the sedimentation potentials set up in non-aqueous liquids until our knowledge of those in aqueous solutions, to which equations of this type do apply, is more complete.

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