60. *Determinations of Electrokinetic Charge and Potential by the Sedimentation Method. Part I. Silica in Aqueous Solutions of Potassium Chloride.*

By C. I. Dulin and G. A. H. Elton.

The sedimentation method for the determination of electrokinetic charges and potentials is applied to the study of fused silica surfaces in dilute aqueous potassium chloride solutions. The results obtained are in good agreement with those calculated from streaming potentials, confirming that the basic assumptions used in deriving the theory of the method are sound. Addition of small amounts of silver chloride to the solutions produces a rise in the charge and a fall in the potential, indicating that the use of silver–silver chloride electrodes in electrokinetic experiments is not to be recommended.

Various methods exist for the determination of electrokinetic potentials, the best known being from measurements of electro-osmosis, streaming potential, and cataphoresis. However, as a general rule, the values of the potential determined for a given system by the different methods are very different (see, *e.g.*, Monaghan, White, and Urban, *J. Physical Chem.*, 1935, **39**, 585; White, Monaghan, and Urban, *ibid.*, p. 611; Rutgers and de Smet, *Trans. Faraday Soc.*, 1945, **41**, 758). The poor agreement is probably due, at least in part, to weakness in the theory of electro-osmosis and of cataphoresis, pointed out recently by Overbeck and Wijga (*Rec. Trav. chim.*, 1946, **65**, 556) and by Booth (*J. Chem. Physics*, 1950, **18**, 1361), respectively. The theory of streaming potential appears to be generally accepted, at least in the case of wide tubes where electroviscosity has little effect (see, *e.g.*, Elton and Hirschler, *Proc. Roy. Soc.*, 1949, *A*, **198**, 581), and the most careful measurements of electrokinetic potentials yet made were probably those of Jones and Wood (*J. Chem. Physics*, 1945, **13**, 106), using the streaming potential method for fused silica surfaces in aqueous potassium chloride solutions.

Recently, a new method has been proposed (Elton, *Proc. Roy. Soc.*, 1949, *A*, **197**, 568; *J. Chem. Physics*, 1951, **13**, 1317) in which the velocity of sedimentation of suspensions of small particles of the solid in the solutions considered is observed. The electrokinetic charge may then be calculated directly from the expression

$$\sigma^2 = g\kappa(u_0 - u)(\rho_2 - \rho_1)/MA_0{}^2uu_0\rho_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ = charge (e.s.u.) per unit area on the particles immersed in the given solution; g = gravitational constant; κ = specific conductivity (e.s.u.) of the suspension; u_0 = rate of settling of the suspension in the absence of electroviscosity (*i.e.*, in a concentrated electrolyte solution); u = rate of settling of the suspension in the given solution; ρ_2, ρ_1 = densities of particles and of solution, respectively; M = mass of particles per ml. of suspension; A_0 = area per g. of particles.

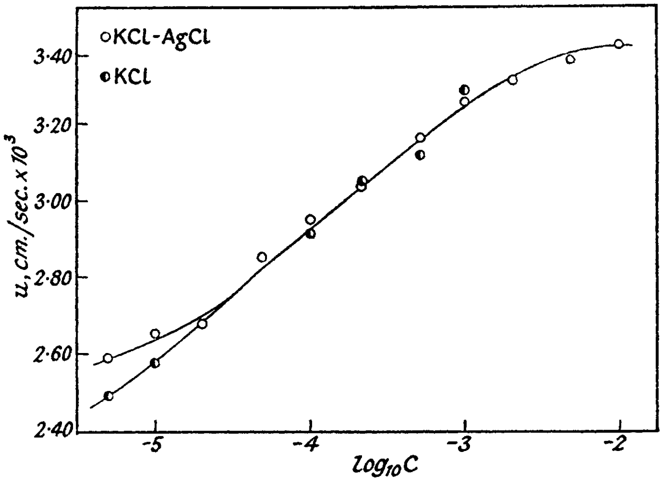
When the charge has been determined, the electrokinetic potential is obtained by using Verwey and Overbeck's expression (" Theory of the Stability of Lyophobic Colloids," 1948, Elsevier Publ. Co. Inc., London), *viz.*,

$$\sigma = \left(\frac{2n\varepsilon kT}{\pi}\right)^{\frac{1}{2}} \sinh\left(\frac{ze\zeta}{2kT}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where n = number of charge-determining ions per ml. of the solution; ε = dielectric constant in the electrical double layer; k = Boltzmann constant; T = absolute temperature; z = valency of charge-determining ion; e = charge on the electron; ζ = electrokinetic potential.

Two difficulties, the first of which is inherent in all electrokinetic calculations, arise in the use of equation (2) : (*a*) ε, the dielectric constant in the double layer may differ from the bulk value of the dielectric constant, owing to the high electric field in the vicinity of the surface, though this effect is likely to be small for solutions of concentration up to about 10^{-3}N (Conway, Bockris, and Ammar, *Trans. Faraday Soc.*, 1951, **47**, 756). (*b*) In aqueous solutions, ions of several kinds may be present, *viz.*, ions of added electrolyte, together with hydrogen and hydroxyl ions, and also bicarbonate ions unless very careful precautions to exclude carbon dioxide are taken. Further ions may be provided by ionisation of the solid surface although this source may be neglected for the purpose of the present paper, where work on fused silica surfaces is to be described. (The case of a solid, *i.e.*, glass, which ionises to some extent, is to be dealt with in a later paper in this series.) The number of hydrogen, hydroxyl, and bicarbonate ions present in conductivity water is small, but at very low concentrations of added electrolyte, say below 10^{-5}N, equation (2) is not strictly applicable, since it was derived for a single electrolyte species.

Sedimentation velocities.



Since an assumption concerning the value of ε is necessary for all calculations of electrokinetic potentials (see Wood, *J. Amer. Chem. Soc.*, 1946, **68**, 432), it would in any case seem preferable to leave all data in terms of electrokinetic charge, a quantity which can be determined unambiguously from measurements of sedimentation velocity, using equation (1). Most data in the literature are, however, given in terms of electrokinetic potential, so in this paper values of both quantities are given. It appears likely from the above discussion that the potentials calculated are reasonably accurate in the concentration range 10^{-5}N to 10^{-3}N, *i.e.*, for most of the range over which electrokinetic measurements are usually required. In order to test this conclusion, determinations have been carried out for the system fused silica–aqueous potassium chloride solution, since silica provides a reproducible surface which is easily cleaned and, as mentioned above, reliable values for the electrokinetic potentials in this system are available for comparison from the work of Jones and Wood. One criticism can, however, be made of this work, *viz.*, that in measuring the streaming potentials, use was made of silver–silver chloride electrodes. Our experiments have shown that these electrodes are not suitable for use in very dilute potassium chloride solutions, as the ionic concentrations may be appreciably increased by dissolution of silver chloride from the electrodes. In order to allow for this, sets of experiments were carried out by use of (i) plain potassium chloride solutions and (ii) potassium chloride solutions saturated with respect to silver chloride.

The sedimentation velocities obtained for a particle-sized specimen of fused silica powder in the two sets of experiments are shown graphically in the figure. In the table, data taken from the smoothed curves have been used to calculate surface charges and potentials, $n = n_{Cl^-}$ being used for the latter calculation; *i.e.*, allowance has been made for the extra ions present in the solutions containing silver chloride. In the table, u_1, κ_1, σ_1, ζ_1, refer to the plain potassium chloride solutions, and u_2, κ_2, σ_2, ζ_2, to the solutions with added silver chloride. Jones and Wood's values are given in the last column. It is seen that the effect of the silver chloride is to raise the charge and lower the potential at low potassium chloride concentrations. The agreement between ζ_2 and Jones and Wood's values is quite good, being of the order of 5%, much better than that usually found between two independent methods. [For example, Rutgers and de Smet (*loc. cit.*) determined ζ for a given glass in potassium chloride solutions from measurements of both streaming potential and electro-osmosis. They found that the latter method gave potentials consistently about 30% lower than the former.]

Concn., N	$\kappa_1 \times 10^6$	$\kappa_2 \times 10^6$	$u_1 \times 10^3$	$u_2 \times 10^3$	$\sigma_1 \times 10^{-2}$	$\sigma_2 \times 10^{-2}$	ζ_1	ζ_2	ζ (J. & W.)
1×10^{-2}	1460·88	1460·88	$3·41_0$	$3·41_0$	77·20	77·20	79·3	79·3	—
5×10^{-3}	730·88	730·88	$3·37_0$	$3·37_0$	65·73	65·73	88·2	88·2	—
2×10^{-3}	292·88	292·88	$3·30_7$	$3·30_7$	51·29	51·29	98·5	98·5	—
1×10^{-3}	146·8	146·8	$3·24_1$	$3·24_1$	42·30	42·30	106·2	106·2	112·5
5×10^{-4}	73·9	73·9	$3·16_0$	$3·16_0$	34·83	34·83	113·8	113·8	—
2×10^{-4}	30·8	30·8	$3·05_9$	$3·05_9$	26·03	26·03	122·3	122·3	—
1×10^{-4}	15·28	15·50	$2·94_3$	$2·94_3$	21·00	21·15	129·0	129·0	133·6
5×10^{-5}	8·18	8·58	$2·85_0$	$2·85_0$	16·85	17·26	135·5	135·3	—
$2·5 \times 10^{-5}$	4·53	5·21	$2·73_8$	$2·73_8$	13·85	14·85	143·2	142·0	—
2×10^{-5}	3·80	4·55	$2·70_2$	$2·70_2$	13·07	14·30	146·0	143·9	—
1×10^{-5}	2·34	3·24	$2·58_4$	$2·64_0$	11·23	12·57	156·0	146·0	142·0
5×10^{-6}	1·51	2·51	$2·46_3$	$2·58_7$	9·795	11·61	167·0	147·6	—
$1 \times$	—	—	$3·50_2$	$3·50_2$	—	—	—	—	—
Water *	—	—	—	—	—	—	—	—	177·0

* See Wood, *J. Amer. Chem. Soc.*, 1946, **68**, 437.

It therefore appears that for the concentration range 10^{-5}N to 10^{-3}N, the only one covered by Jones and Wood's work, the error introduced by setting n in equation (2) equal to the chloride-ion concentration, is small. Further tests, over wider ranges of concentration, are desirable, and are being made by us, but as previously mentioned, few reliable data for comparison are available. The good agreement between the results obtained from streaming potential and sedimentation velocity is some confirmation that the theoretical basis of the methods is sound. The latter method is a simple one to carry out experimentally, provided that the material to be studied is obtainable in powder form in sufficient quantity to permit the extraction of a 50—100 mg. sample of uniform particle size.

Finally, we may conclude from the differences obtained in the two sets of experiments that for electrokinetic measurements, the use of silver–silver chloride electrodes is not to be recommended, at least in dilute solutions. This was realised by Wood and Robinson (*J. Chem. Physics*, 1946, **14**, 258), who used bright platinum electrodes for their measurements on silica in dilute solutions of barium chloride.

EXPERIMENTAL

Materials.—Fused silica powder was supplied by Messrs. Thermal Syndicate Ltd. It was cleaned by repeated boiling with aqua regia, and washed many times with conductivity water. The water used throughout these experiments had a conductivity of 0·6—0·8 gemmho, similar to that used by Jones and Wood. Potassium chloride was obtained by recrystallising the "AnalaR" salt several times from conductivity water. Silver chloride was prepared from recrystallised "AnalaR" silver nitrate by reaction in dilute solution with the calculated quantity of potassium chloride, washed thoroughly, and used immediately.

Particle Sizing of Silica.—This was done by fractional sedimentation in a number of large shallow pans followed by a similar process in measuring cylinders. The specimen used in the experiments described, weighing about 70 mg., was separated from about 100 g. of powder. It formed a suspension which sedimented at a uniform rate, giving a sharp settling meniscus with a limiting rate of fall, in concentrated solutions, of $3 \cdot 50 \times 10^{-3}$ cm./sec.

Sedimentation Experiments.—The specimen of silica was suspended in 100 ml. of aqueous potassium chloride solution, and the sedimentation experiments carried out as described previously (Elton, 1949, *loc. cit.*), in a thermostat at $25 \cdot 00° \pm 0 \cdot 01°$. Solutions were prepared by successive dilution, after the suspension had been allowed to settle out, at least two determinations being made at each concentration. The weight of particles per ml. in the suspension was determined at the completion of the series by centrifuging and weighing on a microbalance: $M = 6 \cdot 765 \times 10^{-4}$ g./ml.

Surface-area Determination.—This was done by a modification of the catalytic decomposition method described by Elton and MacDougall (*J. Soc. Chem. Ind.*, 1946, **65**, 212). A known weight of the particles was given a very thin continuous coating of metallic silver by stirring them for ten minutes in ammoniacal 4% silver nitrate solution at 60—70°. The silvered particles were then washed, with centrifuging, and transferred to a flask containing 100 ml. of a borax buffer solution of pH 9·7 in a thermostat at 25·00°. The suspension of particles was stirred, and 25 ml. of 0·1N-hydrogen peroxide solution at 25·00° rapidly introduced into the flask. At the end of 100 seconds, the reaction was stopped by the addition of an excess of 2N-sulphuric acid, and the hydrogen peroxide remaining determined by titration with permanganate. The rate of decomposition of the peroxide is directly proportional to the surface area of silver present. The method was standardised by using a silvered specimen of glass microspheres, prepared by Bloomquist and Clark's method (*Ind. Eng. Chem. Anal.*, 1940, **12**, 61), and accurately particle-sized by the method described above. Determinations of limiting settling rate and weight per ml. of a suspension of the glass spheres gave their mean radius and area per g. The surface area of the silica was then obtained by comparing the rates of decomposition of the peroxide by the two silvered materials. Area per g. $(A_0) = 1 \cdot 234 \times 10^4$ cm.^{2}.

BATTERSEA POLYTECHNIC, S.W.11.

[*Received, September* 12*th*, 1951.]