

564. *Determinations of Electrokinetic Charge and Potential by the Sedimentation Method. Part II.* Pyrex Glass in Aqueous Potassium Chloride Solutions.*

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The sedimentation velocity method for the determination of electrokinetic charges and potentials is applied to the study of Pyrex-glass surfaces in dilute aqueous potassium chloride solutions, (a) Pyrex powder, consisting of irregularly shaped particles, and (b) microspheres being used. The good agreement obtained between results with these different particles is further support for the validity of the sedimentation equation for non-spherical particles. The presence of a small amount of silver chloride in the solutions is shown to produce, for low potassium chloride concentrations, a considerable increase in charge, confirming previous conclusions on the unsuitability of silver-silver chloride electrodes for electrokinetic use.

IN connection with an experimental study of the surface conductivity of Pyrex-glass surfaces in aqueous potassium chloride solutions, to be described elsewhere, it became necessary to determine the electrokinetic charge σ carried by Pyrex surfaces in such solutions. This has been done by using the method of electroviscous sedimentation (see Elton, *J. Chem. Physics*, 1951, **19**, 1317; Dulin and Elton, Part I *) and the opportunity has been taken of further testing the theory of the method by comparing results obtained with irregularly shaped particles of ground Pyrex with those using Pyrex microspheres prepared by the method of Bloomquist and Clark (*Ind. Eng. Chem. Anal.*, 1940, **12**, 61). In addition, since some of the surface conductance measurements had involved the use of silver-silver chloride reversible electrodes, it was necessary to assess the effect of any dissolution of silver chloride from these electrodes on the charge carried by the Pyrex surface. For this reason, two sets of sedimentation experiments were carried out, (i) plain potassium chloride solutions, and (ii) potassium chloride solutions saturated with respect to silver chloride being used.

Calculation of the electrokinetic charges from the sedimentation velocity results for non-spherical particles was made, as in Part I, from the equation

$$\sigma^2 = g\kappa(\rho_2 - \rho_1)(u_0 - u)/MA_0^2\rho_2uu_0 \dots \dots \dots (1)$$

where g is the gravitational constant, ρ_2 and ρ_1 are the densities of glass and solution respectively, κ the specific conductivity of the suspension, M the mass of particles per ml., A_0 their area per g., u the velocity of sedimentation of the suspension in a given solution, and u_0 the limiting rate of settling, measured in concentrated electrolyte solutions. For spherical particles equation (1) simplifies to

$$\sigma^2 = \rho_2\eta\kappa(u_0 - u)/2Mu \dots \dots \dots (2)$$

where η is the viscosity of the solution. The electrokinetic potential ζ may then be calculated by using the equation

$$\sigma = \left(\frac{2n\epsilon kT}{\pi}\right)^{\frac{1}{2}} \sinh\left(\frac{ze\zeta}{2kT}\right) \dots \dots \dots (3)$$

where ϵ is the dielectric constant in the diffuse part of the double layer (see Part I), k is the Boltzman constant, e the charge on the electron, T the absolute temperature, and n the number of charge-determining ions, of valency z , per ml. of solution. As pointed out in Part I, n includes ions supplied by the water and also, in the case of glass, by ionisation of the surface. In the suspensions used, the contribution of such ions to the total conductivity was found to be consistently 4—5 gemmhos (see Hirschler, Thesis, London, 1951), the estimated contribution to n being about 3×10^{15} . In our calculations this amount has

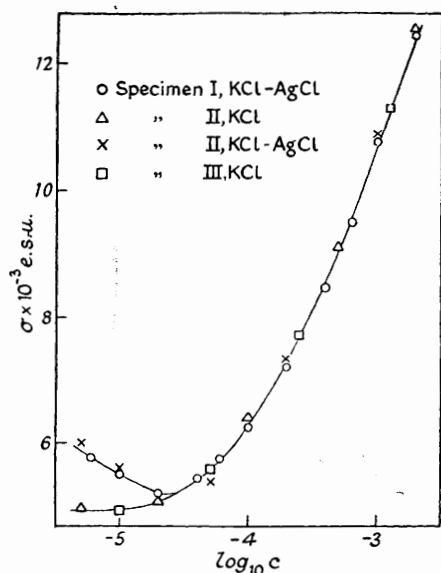
* Part I, *J.*, 1952, 286.

been added to the potassium chloride concentration to give the final value of n . In view of the fairly large value of this correction factor, values of ζ are only given for potassium chloride solutions of $10^{-4}N$ and higher concentrations. In fact, it is found from the form of equation (3) that for a given surface charge, the calculated potential is not very sensitive to the value of n taken, the 30% correction to n applied for the $10^{-4}N$ -solution leading to only a 3% correction in ζ .

The figure shows the results obtained for σ , with two specimens of microspheres and one specimen of Pyrex powder, the agreement between the results obtained from these different batches being very good. The table gives the value of charge, taken from the graph, for a

KCl, N	2×10^{-3}	1×10^{-3}	5×10^{-4}	2×10^{-4}	1×10^{-4}	5×10^{-5}	2×10^{-5}	1×10^{-5}	5×10^{-6}
$\sigma_1 \times 10^{-3}$, e.s.u./cm. ²	12.41	10.80	9.09	7.21	6.23	5.53	5.14	4.98	4.88
$\sigma_2 \times 10^{-3}$, e.s.u./cm. ²	12.41	10.80	9.09	7.21	6.23	5.53	5.22	5.47	5.90
ζ , mv.....	142	152	161	170	178	—	—	—	—

number of concentrations, σ_1 being the charge in plain potassium chloride solutions, and σ_2 that in solutions saturated with respect to silver chloride. Calculated values of ζ for



potassium chloride concentrations of $10^{-4}N$ and over are given in the final line. As was the case for silica in potassium chloride solutions (see Part I), the effect of added silver chloride is to raise the charge at low potassium chloride concentrations, where the dissociation of the silver chloride becomes appreciable. The effect is rather more marked for glass, the charge actually rising with dilution below a potassium chloride concentration of about $3 \times 10^{-5}N$. These results confirm our previous conclusions that, wherever possible, the use of silver-silver chloride electrodes is to be avoided in electrokinetic measurements, especially in very dilute solutions. In the absence of silver chloride, the charge per cm.² tends at low concentrations to a lower limiting value of about 4700 e.s.u. (compare the corresponding value of about 600 e.s.u. for silica). The extra charge is presumably due, at least in part, to the ionisation of the glass. The difference in charge per cm.² between glass and silica remains at about 4000 e.s.u. up to about $10^{-4}N$, where the

values to the nearest hundred e.s.u. are 6200 and 2100 e.s.u., respectively, then increases steadily, the values at $10^{-3}N$ being 10,800 and 4200 e.s.u.

No reliable values of the electrokinetic potentials of Pyrex appear to be available in the literature for comparison with those given in the table. The figures quoted by Urban, White, and Strassner (*J. Phys. Chem.*, 1935, **39**, 311), calculated from Lachs and Biczky's streaming-potential measurements (*Z. physikal. Chem.*, 1930, **A**, **148**, 441), show a maximum in the ζ - c graph, which, as shown by Rutgers (*Trans. Faraday Soc.*, 1940, **36**, 69), is due to failure to allow for the effect of surface conductance on the measurements, an omission which may easily cause errors of 100 mv in the values of ζ obtained. The most reliable values for the electrokinetic potentials of a glass are probably those of Rutgers (*loc. cit.*) for Jena 16^{III} glass, the potentials of which are little different from those found by us for Pyrex; e.g., for the Jena glass in $10^{-4}N$ -potassium chloride solution, a value of 165 mv was obtained (compare our value for Pyrex of 178 mv).

EXPERIMENTAL

Materials.—(i) Pyrex glass powder was prepared by grinding clean Pyrex glass in a mortar, followed by ball milling in an all-porcelain mill for several hours. Particles in the size range 2–5 microns were then separated by fractional sedimentation. They were cleaned by treat-

ment with several changes of 18% hydrochloric acid, then with boiling nitric acid and aqua regia, and finally washed many times with conductivity water. (All water used in this investigation was "equilibrium" conductivity water, of specific conductivity about 0.8 gemmho.) The milling process produced a small amount of very fine, near-colloidal porcelain dust, which was easily removed from the glass in the fractional sedimentation process. (ii) Pyrex microspheres were made by Bloomquist and Clark's method (*loc. cit.*), in which a fine dust of Pyrex particles is introduced into the air stream of a blowpipe, and blown through the flame. After formation, they were cleaned as described above. Particle sizing of powder and microspheres was carried out as described in Part I (see also Hirschler, Thesis, *loc. cit.*).

Potassium chloride and silver chloride were prepared in a pure state as described in Part I. All vessels used were treated with alcohol-nitric acid and thoroughly steamed immediately before use.

Sedimentation velocities for the suspensions were determined as described by Elton (*Proc. Roy. Soc.*, 1949, A, **197**, 568), a thermostat at $25.00^\circ \pm 0.01^\circ$ being used. The mass of particles per ml. of suspension was determined in each case at the conclusion of the set of experiments by weighing on a microbalance. Limiting rates of settling (u_0) and mass per ml. (M) were: Specimen I (microspheres) $3.46_9 \times 10^{-4}$ cm./sec., 5.90×10^{-4} g./ml.; Specimen II (microspheres) $3.19_7 \times 10^{-4}$ cm./sec., 8.22×10^{-4} g./ml.; Specimen III (powder) $3.80_5 \times 10^{-3}$ cm./sec., 4.50×10^{-4} g./ml.

Surface-area determination for Specimen III was done as described in Part I, the method of catalytic decomposition of hydrogen peroxide being used: $A_0 = 7.81 \times 10^3$ cm.²/g.

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