233. *Determination of Electrokinetic Charge and Potential by the Sedimentation Method. Part III.* Silica in Some Aqueous Chloride Solutions.*

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The sedimentation method is used to determine the electrokinetic charges and potentials of fused silica surfaces in dilute aqueous solutions of various chlorides. Although the results for potassium chloride agree well with those obtained from streaming-potential measurements, yet those for chlorides with higher-valency cations differ to some extent. Possible reasons for these deviations are discussed.

THE sedimentation method (Elton, *Proc. Roy. Soc.*, 1949, A, **197**, 568; *J. Chem. Physics*, 1951, **13**, 1317; Dulin and Elton, Part I; * Elton and Hirschler, Part II *) enables the calculation of the electrokinetic charge from the velocity of sedimentation of a suspension of small particles from the expression

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

where σ is the net charge per unit area in the diffuse part of the double layer at the particle–liquid interface, $\boldsymbol{g}$ the gravitational constant, κ the specific conductivity of the suspension, u_0 the rate of settling of the suspension in the absence of electroviscosity (*i.e.*, in a concentrated electrolyte solution), u the analogous rate in the given solution, ρ_1 and ρ_2 are the densities of solution and particle respectively, M is the mass of particles per ml. of suspension, and A_0 the area per g. of the particles.

Once this charge has been obtained, the electrokinetic potential ζ may be determined for binary electrolyte solutions of normality c from the expression

$$\sigma = \left(\frac{N\varepsilon\boldsymbol{k}Tc}{2\pi}\right)^{\frac{1}{2}}\left\{\frac{1}{z_-}[\exp(z_-\boldsymbol{e}\zeta/\boldsymbol{k}T) - 1] + \frac{1}{z_+}[\exp(-z_+\boldsymbol{e}\zeta/\boldsymbol{k}T) - 1]\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad 2)$$

given by Verwey and Overbeek (" Theory of the Stability of Lyophobic Colloids," 1948, Elsevier Publ. Co., Inc., London). In equation (2), $\boldsymbol{N}$ is the Avogadro number, ε the dielectric constant in the double layer, $\boldsymbol{k}$ the Boltzmann constant, T the absolute temperature, z_+ and z_- are the valencies of cation and anion respectively, and $\boldsymbol{e}$ is the charge on the electron.

For solutions containing more than two ionic species, a more complicated expression has to be used, *viz.*

$$\sigma = \left(\frac{N\varepsilon\boldsymbol{k}T}{2\pi}\right)^{\frac{1}{2}}\left\{\Sigma\frac{c_r}{z_r}[\exp(z_r\boldsymbol{e}\zeta/\boldsymbol{k}T) - 1] + \Sigma\frac{c_s}{z_s}[\exp(-z_s\boldsymbol{e}\zeta/\boldsymbol{k}T) - 1]\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (3)$$

where the summation terms are those of the negative and positive ions respectively, c_r and c_s are the normalities of the ions of valency $(z_r)_-$ and $(z_s)_+$, respectively.

In solutions of chlorides of the higher-valency metals, hydrolysis often occurs, especially in very dilute solutions, resulting in the removal of multivalent cations and their replacement by an equivalent number of hydrogen ions. In calculating the electrokinetic potential from the charge, this fact must be taken into account. If the charge and potential are positive, the positive-ion summation term in equation (3) is negligible, except for very low values of ζ. Consequently, the effect of hydrolysis on the calculated value of the potential is generally small in cases where the charge is positive. For negative charges and potentials, however, the positive-ion summation term in (3) is the more important, and changes in electrolyte concentration produced by hydrolysis are important, and must be allowed for so far as is possible. It may be said, in general, that for a given surface charge, the behaviour of the counter-ions is the important factor in determining the electrokinetic potential.

Measurements were made of the sedimentation velocities of homodisperse suspensions of fused silica powder in dilute aqueous solutions of chlorides of sodium, hydrogen, barium,

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* Part I, *J.*, 1952, 286; Part II, *J.*, 1952, 2953.

magnesium, lanthanum, and thorium, data from smoothed velocity–concentration curves being taken for the calculation of charges and potentials. The tables give the results obtained for these solutions (three in detail), some of which have been studied by Jones and Wood (*J. Chem. Physics*, 1945, **13**, 106) and by Wood and Robinson (*ibid.*, 1946, **14**, 258; *J. Amer. Chem. Soc.*, 1947, **69**, 1862), using in each case the streaming-potential method. Most of the measurements of these workers involved the use of silver–silver chloride reversible electrodes, a fact which produced errors of a few millivolts in their results (see Part I), owing to contamination of the solution by traces of electrolyte leached from the electrodes.

Summary of results for all solutions.

	σ, e.s.u./cm.^{2}						ζ, mv					
c	NaCl	HCl	$BaCl_2$	$MgCl_2$	$LaCl_3$	$ThCl_4$	NaCl	HCl	$BaCl_2$	$MgCl_2$	$LaCl_3$	$ThCl_4$
2×10^{-3}	5289	4434	—	—	3342*	—	100·0	91·3	—	—	77·0*	—
1×10^{-3}	4331	3493	887	—	472*	3142*	106·2	96·6	25·9	—	18·0*	90·8*
5×10^{-4}	3470	2781	1034	345	0	3876*	113·7	102·5	36·2	16·2	0·0	119·1*
2×10^{-4}	2528	2090	1132	745	361	2066*	121·8	112·0	49·2	39·2	19·4	118·3*
1×10^{-4}	1990	1689	1082	809	496	1229*	126·5	117·9	59·5	49·4	28·4	105·0*
5×10^{-5}	1581	1379	922	784	530	723*	132·2	125·3	61·3	57·2	36·5	92·3*
2×10^{-5}	1201	1096	791	718	467	327*	141·6	137·0	72·0	66·6	42·5	75·8*
1×10^{-5}	1040	991	674	639	441	159*	151·8	143·8	74·4	72·4	47·8	58·1*
5×10^{-6}	—	—	600	596	447	47*	—	—	79·8	79·6	54·6	24·6*
2×10^{-6}	—	—	553	552	477	96	—	—	89·5	89·4	63·7	26·8
1×10^{-6}	—	—	548	563	—	333	—	—	98·2	98·9	—	46·4

All values are negative except those marked *.

c	$u \times 10^3$, cm./sec.	$10^6\kappa$	σ, e.s.u./cm.^{2}	ζ, mv	ζ Wood,* interp'd	c	$u \times 10^3$, cm./sec.	$10^6\kappa$	σ, e.s.u./cm.^{2}	ζ, mv	ζ Wood,* interp'd
Results for $BaCl_2$.											
1×10^{-3}	$2{\cdot}88_6$	136·0	−887	−25·9	−45·0	2×10^{-5}	$2{\cdot}39_2$	3·66	−791	−72·0	−98·0
5×10^{-4}	$2{\cdot}88_0$	67·11	−1034	−36·2	−58·0	1×10^{-5}	$2{\cdot}30_0$	2·16	−674	−74·4	−103·5
2×10^{-4}	$2{\cdot}74_7$	27·68	−1132	−49·2	−70·0	5×10^{-6}	$2{\cdot}22_0$	1·58	−600	−79·8	−109·0
1×10^{-4}	$2{\cdot}64_3$	14·73	−1082	−59·5	−79·0	2×10^{-6}	$2{\cdot}13_1$	1·05	−553	−89·5	−120·0
5×10^{-5}	$2{\cdot}53_2$	7·21	−922	−61·3	−88·0	1×10^{-6}	$2{\cdot}08_0$	0·95	−548	−98·2	—
Results for $LaCl_3$.											
2×10^{-3}	$2{\cdot}88_2$	323·60	+3342	+77·0	—	5×10^{-5}	$2{\cdot}79_4$	8·71	−530	−36·5	−27·0
1×10^{-3}	$2{\cdot}90_2$	162·20	+472	+18·0	+12·5	2×10^{-5}	$2{\cdot}69_0$	3·39	−467	−42·5	—
5×10^{-4}	$2{\cdot}90_7$	75·86	0	0	−7·5	1×10^{-5}	$2{\cdot}59_1$	2·00	−441	−47·8	—
2×10^{-4}	$2{\cdot}89_2$	31·62	−361	−19·4	−16·0	5×10^{-6}	$2{\cdot}47_8$	1·45	−447	−54·6	—
1×10^{-4}	$2{\cdot}85_5$	16·98	−496	−28·4	−22·0	2×10^{-6}	$2{\cdot}17_6$	0·87	−477	−63·7	—
Results for $ThCl_4$.											
1×10^{-3}	$2{\cdot}74_6$	208·90	+3142	+90·8	+141·0	2×10^{-5}	$2{\cdot}84_2$	5·89	+327	+75·8	+126·0
5×10^{-4}	$2{\cdot}48_0$	109·60	+3876	+119·1	+158·0	1×10^{-5}	$2{\cdot}87_8$	3·16	+159	+58·1	+96·0
2×10^{-4}	$2{\cdot}61_4$	47·86	+2066	+118·3	+175·0	5×10^{-6}	$2{\cdot}90_3$	2·04	+47	+24·6	+57·5
1×10^{-4}	$2{\cdot}70_7$	25·70	+1229	+105·0	+177·0	2×10^{-6}	$2{\cdot}88_3$	1·38	−96	−26·8	—
5×10^{-5}	$2{\cdot}77_5$	13·80	+723	+92·3	+164·0	1×10^{-6}	$2{\cdot}61_2$	1·23	−333	−46·4	—

* Interpolated from Wood's data (*loc. cit.*).

In order to verify that the results obtained by the sedimentation method were independent of particle size and suspension concentration over the range used (already verified for glass particles, see Part I, *loc. cit.*), measurements were made on two widely different suspensions in dilute hydrochloric acid, the final values of ζ obtained being in agreement to within about one millivolt at all electrolyte concentrations studied. This confirms that in our experiments, using suspensions with volume fractions of solid of the order of 10^{-3} to 10^{-4}, particle–particle interaction is negligible (see also Oseen, *Ark. Mat. Astron. och. Fysik*, 1911, **7**, 33; Faxen, *ibid.*, 1925—1927, **19**, *a*, 13; Smoluchowski, *Bull. Acad. Sci. Cracovie*, 1911, **1**, *a*, 28; Stimson and Jeffrey, *Proc. Roy. Soc.*, 1926, *A*, **111**, 110). In view of this finding, measurements on the other chloride solutions were made on a single suspension, at least two runs being made at each concentration.

Discussion.—It is seen that the results for sodium chloride solutions are closely similar to those obtained previously for potassium chloride, the difference in charge being small, and in potential negligible. The fact that the nature of the univalent cation has little effect on the electrokinetic properties indicates that they probably possess rather low specific chemical adsorption potentials at the interface, and play only a small part in the construction of the fixed part of the double layer.

With hydrogen chloride solutions, however, the charge is lower throughout, the difference being fairly constant and of the order 400—700 e.s.u. over a wide range. A difference is to be expected, since in the salt solutions there occurs adsorption into the fixed part of the double layer of hydroxyl and, more important, bicarbonate ions from the conductivity water, whilst in acid solutions these foreign ions will be very largely suppressed, giving a negative charge in the fixed part of the double layer due almost entirely to chloride ions. The difference between the charge in sodium or potassium chloride solutions and that in hydrogen chloride will probably be about equal to the charge carried by silica in the pure solvent, it being assumed that the charges are approximately additive. By extrapolating results to high dilution, a value of the charge in equilibrium water of about 530—550 e.s.u. has been obtained, in agreement with the observed difference between the charge in the salt and in acid solutions. At very low concentrations the difference becomes rather smaller as the degree of suppression of the bicarbonate ions decreases. The effect occurs at a slightly higher concentration than would be expected on this basis alone, possibly indicating that the assumption that the charges are additive is only valid approximately in this range.

For both magnesium and barium chloride solutions the charges and potentials are lower than for the chlorides of univalent cations, owing to the increased ease with which the bivalent cations are taken into the fixed part of the double layer. The charges and potentials for the magnesium chloride solutions are somewhat lower than for barium chloride, especially at the higher concentrations. The accuracy of the measurements is lower for these concentrations, owing to electroviscosity being rather small, and the sedimentation meniscus less sharp, but the differences are considerably greater than the experimental error. This presumably indicates that the specific chemical adsorption potential of the magnesium ion is significantly greater than that of the barium ion, so that magnesium ions are more easily adsorbed into the fixed part of the double layer, with a consequent lowering of charge and potential. The values of ζ obtained by us for barium chloride are lower by about 20% than those of Wood and Robinson (*loc. cit.*). This discrepancy is considerably greater than that found for potassium chloride, where the difference between the results from the two methods was never greater than 5%, after allowance for the effect of contamination of the solutions by leaching fron the electrodes in the streaming-potential measurements. Some possible reasons for the observed difference are discussed below.

Preferential adsorption of a high-valent cation into the fixed layer is shown to a greater extent by lanthanum chloride, for which the charge reaches zero at a concentration of 5×10^{-4}N, becoming positive at higher concentrations. The values of ζ are small throughout the range studied and differ by only a few mv from those of Wood and Robinson (*loc. cit.*). Corrections for the change in concentration brought about by hydrolysis were made in calculating ζ from equation (3).

Thorium chloride shows a negative charge and potential at very high dilutions, reaching zero at a concentration of about $3—4 \times 10^{-6}$N, and becoming positive at higher concentrations. The positive charge rises to a maximum value at a concentration of about 4×10^{-4}N, then falls away towards zero. The velocity–concentration curve is of rather complicated shape for thorium chloride. As the concentration is lowered from high values, the velocity falls from its limiting value, reaching a minimum at the concentration of maximum charge. The velocity then rises to the limiting value again, passing through a maximum at the concentration of zero charge, then decreasing again fairly sharply. Once again, allowance had to be made for the effect of hydrolysis in calculating ζ from equation (3). The results obtained show the same trends with concentration as those of Wood and Robinson, but the quantitative agreement is not good, differences in ζ of up to 35% being found.

Various possible causes of the observed differences in solutions of chlorides of the multivalent metals may be considered. First, contamination of the solutions by silver chloride from the electrodes in the streaming-potential experiments can produce errors of 20 mv or even more in very dilute solutions (see Part I, *loc. cit.*), but the dissociation of the silver chloride should be largely suppressed at concentrations much above 10^{-5}N, and, furthermore, this contamination would probably bring about a lowering of ζ, while in practice the streaming-potential results are generally found to be rather higher than those for sedimentation velocity.

In calculating ζ from experimental results, the dielectric constant in the diffuse part of the double layer is involved (see Part I). It is known that the value of ε in this layer may differ considerably from that of the bulk solution (see Conway, Bockris, and Ammar, *Trans. Faraday Soc.*, 1951, **47**, 756). In the streaming potential equation

$$\zeta = -4\pi\eta E\kappa/\varepsilon P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where η is the viscosity of the solution, P the applied pressure, and E the streaming potential, the value of ζ obtained from a given set of experimental data depends linearly on ε, while in calculations of ζ from equation (3) for sedimentation experiments ε is involved logarithmically. If the bulk value of the dielectric constant is used in each case, therefore, the two sets of results for ζ will differ if this value is the incorrect one for use in the double layer. The fact that the two sets agree quite well for a uni-univalent electrolyte therefore appears to indicate that the appropriate mean value for ε in the diffuse layer in this case is not far different from the bulk value for potentials of this magnitude. Bigger deviations from the bulk value, are, however to be expected in solutions containing multivalent cations (Conway, Bockris, and Ammar, *loc. cit.*), but a simple calculation shows that this should produce lower values of ζ by the streaming-potential method, while in fact the reverse is the case.

It appears most probable that the difference arises from the difficulty in assessing accurately the concentration of each ionic species in a solution of a multivalent metal chloride. In addition to hydrolysis direct to undissociated base with consequent liberation of hydrogen ions, which can be allowed for in terms of the known dissociation constant of the base, other products of partial and complete hydrolysis will be formed. For example, in the case of thorium chloride various partially hydrolysed ions will exist, *e.g.*, $Th(OH)^{+++}$ etc., and in addition thorium hydroxide occurs as positively charged colloidal micelles, the adsorption properties of which are not known. These facts serve to emphasise our previous remarks (Parts I and II) that it is preferable to leave the data in the form of the charge, which can be calculated directly from experimentally measured quantities. Conversion of the charge figures into potentials gives reliable results for uni-univalent electrolytes, but for the higher valencies, the potentials, although of the right order and showing the correct trends with concentration, are probably of rather low accuracy.

EXPERIMENTAL

Materials.—Fused silica powder was cleaned and particle-sized as described in Part I. The water used throughout was equilibrium conductivity water of specific conductivity about 0·8 gemmho. Sodium, barium, and magnesium chlorides were obtained by appropriate recrystallisations of the " AnalaR " salts. Hydrochloric acid was obtained by redistillation of the " AnalaR " acid. Lanthanum chloride was a spectroscopically pure sample supplied in solution by Messrs. Johnson, Matthey and Co., Ltd.; a pure sample of thorium chloride was prepared by Kremer's method (*J. Amer. Chem. Soc.*, 1942, **64**, 1009). All vessels used were treated with alcohol–nitric acid and thoroughly steamed before use.

Sedimentation Experiments.—These were carried out as described previously (Elton, 1949, *loc. cit.*), in a thermostat at 25·00° ± 0·01°. Solutions were prepared by successive dilution, after the suspension had been allowed to settle out. The suspension used throughout, except for the duplicate run with hydrogen chloride solutions, had a surface area per g. (A_0) of $1{\cdot}40_3 \times 10^4$ cm.^{2}, mass per unit volume (M) of $1{\cdot}20_2 \times 10^{-3}$ g./ml., and limiting rate of sedimentation, in concentrated electrolyte solutions (u_0), of $2{\cdot}90_7 \times 10^{-3}$ cm./sec. The suspension used for the duplicate run with hydrogen chloride solutions had $A_0 = 2{\cdot}65_6 \times 10^4$ cm.^{2}, $M = 3{\cdot}14_1 \times 10^{-4}$ g./ml., and $u_0 = 3{\cdot}24_7 \times 10^{-3}$ cm./sec. (Surface areas were determined by the method of catalytic decomposition of hydrogen peroxide, as described in Part I.)

In solutions where the electrokinetic potential was low, the sedimentation meniscus was less sharp than usual, owing to a smaller electroviscous sharpening effect (see Elton, 1951, *loc. cit.*). Also, in such solutions, especially where ζ was less than about 30 mv there was a marked tendency for the particles to undergo some coagulation after the suspension had settled out and stood for a while. When this occurred, the suspension could be returned to its normal state by vigorous mechanical shaking for an hour or more.

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[*Received, October* 17*th*, 1952.]