# 428. *Determinations of Electrokinetic Charge and Potential by the Sedimentation Method. Part IV.* Silica in Conductivity Water.*

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The sedimentation-velocity method for the determination of electrokinetic charge and potential is applied to the study of fused silica surfaces in conductivity water of various qualities. Contrary to reports by some previous workers, a systematic trend is found in the value of these quantities with the conductivity of the water.

DETERMINATIONS of the electrokinetic charge and potential at the silica–potassium chloride solution, silica–sodium chloride solution, and silica–hydrochloric acid solution interfaces (Parts I and III *) have shown that, at corresponding concentrations in the range $5 \times 10^{-5}$N—$2 \times 10^{-5}$N, although the charges and potentials in potassium chloride and sodium chloride solutions are closely similar, yet those in the acid are considerably lower. This difference in the charge is about 250 e.s.u. at $5 \times 10^{-5}$N and increases to about 750 e.s.u. at $2 \times 10^{-3}$N. At concentrations below $2 \times 10^{-5}$N, the charge and potential become very similar at all three interfaces.

The solutions used in these experiments were made up in " equilibrium water," *i.e.*, conductivity water which had been allowed to come into equilibrium with the atmosphere. The conductivity of this water was of the order 1 gemmho, depending on atmospheric conditions, and may be attributed (see, *e.g.*, Davies, " Conductivity of Solutions," Chapman and Hall, London, 1933) to hydrogen and bicarbonate ions provided by dissociation of carbonic acid formed from dissolved carbon dioxide.

The concentration ($2$—$5 \times 10^{-5}$N) at which the difference ($\Delta\sigma$) between the charge in the salt solutions from that in the acid solution becomes appreciable is approximately the concentration at which ionisation of dissolved carbonic acid becomes negligible in acid solutions. It might, therefore, be suggested that a charge exists at the silica–water interface due to adsorption of bicarbonate ions (and/or OH′, $CO_3''$), this charge persisting when a neutral salt is added to the system but being stripped off by a sufficient concentration of acid. In a salt solution the charge due to bicarbonate ion (and/or OH′, $CO_3''$) will depend on the magnitude of the affinity of these ions for the surface (adsorption potential) and the repulsion owing to the negative electrical potential at the surface. As this electrical potential is made less negative by increased salt concentration, the repulsion will be reduced, and it is to be expected that the contribution to the charge of the bicarbonate ion (and/or OH′, $CO_3''$) will be larger. This may account in part for the increased value of $\Delta\sigma$ as the concentration is increased. Furthermore, although a solution, $2 \times 10^{-5}$N with respect to acid, may contain a sufficiently small number of bicarbonate, hydroxyl, and carbonate ions to render their contribution to the conductivity negligible, these ions may still make an appreciable contribution to the charge if they possess large adsorption potentials. Hence,

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* Parts I, II, and III, *J.*, 1952, 286, 2953; 1953, 1168.

from the point of view of the surface, a concentration of acid greater than 2 × $10^{-5}$N may be needed to render the effect of bicarbonate, hydroxyl, and carbonate ions completely negligible.

The experimental work described here was carried out in order to investigate the charge and potential at the silica–water interface and any systematic variation of these quantities with the carbonic acid content of the water. The sedimentation velocities of a particle-sized specimen of fused silica powder were measured in water of various qualities, *i.e.*, carbon dioxide content. The electrokinetic charges, $\sigma$, at the interface were calculated by the expression

$$\sigma^2 = \frac{g\kappa(u_0 - u)(\rho_2 - \rho_1)}{MA_0^2uu_0\rho_2}$$

where $g$ = gravitational constant, $\kappa$ = specific conductivity (e.s.u.) of the suspension, $u_0$ and $u$ = rate of settling of the suspension in concentrated electrolyte solutions, *i.e.*, in absence of electroviscosity and in a given solution respectively; $\rho_2$, $\rho_1$ = densities of silica and solution respectively; $M$ = mass of particles per ml. of suspension; $A_0$ = area per g. of particles.

The results given in the Tables and the Figures show that the velocity of sedimentation is close to the limiting velocity in water of high purity and decreases markedly as the water becomes equilibrated with the atmosphere. The charge is seen to rise from 125 e.s.u. in the purest water obtained to somewhat over 500 e.s.u. in water of conductivity 1 gemmho.

FIG. 1.

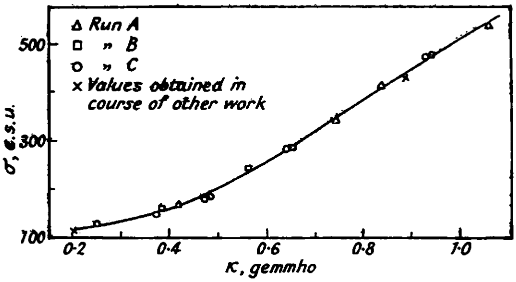
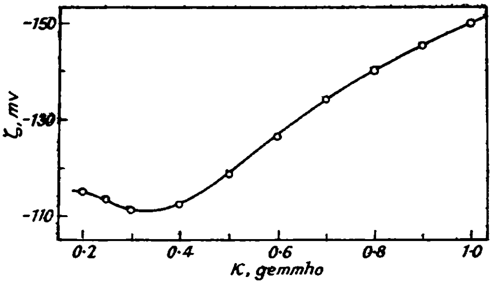


FIG. 2.



| $\kappa$, gemmho | $u$, cm./sec. × $10^3$ | Charge $\sigma$, e.s.u. | $\kappa$, gemmho | $u$, cm./sec. × $10^3$ | Charge $\sigma$, e.s.u. | $\kappa$, gemmho | $u$, cm./sec. × $10^3$ | Charge $\sigma$, e.s.u. |
|---|---|---|---|---|---|---|---|---|
| *Runs A* and *B*: Mass of silica per ml. of suspension = 8·096 × $10^{-4}$ g., area per g. of silica = 1·20 × $10^4$ sq. cm., limiting velocity = 3·497 × $10^{-3}$ cm./sec. | | | | | | | | |
| 0·3843 | 3·337 | 157·6 | 0·5616 | 3·245 | 241·2 | 0·8345 | 3·000 | 409·0 |
| 0·4173 | 3·317 | 165·5 | 0·6497 | 3·187 | 284·6 | 0·9358 | 2·924 | 471·1 |
| 0·4709 | 3·333 | 167·4 | 0·7240 | 3·100 | 339·0 | 1·056 | 2·863 | 532·0 |
| *Run C*: Mass of silica per ml. of suspension = 5·740 × $10^{-4}$ g., area per g. of silica = 1·40 × $10^4$ sq. cm., limiting velocity = 3·033 × $10^{-3}$ cm./sec. | | | | | | | | |
| 0·2495 | 2·905 | 126·0 | 0·4836 | 2·896 | 181·8 | 0·9240 | 2·604 | 469·0 |
| 0·3696 | 2·916 | 146·4 | 0·6376 | 2·795 | 280·1 | | | |

| $\kappa$, gemmho | $\sigma$, e.s.u. | $n_H = n_{HCO_3} + n_{OH}$, ions/ml. × $10^{-14}$ | $\zeta$, mv | $\kappa$, gemmho | $\sigma$, e.s.u. | $n_H = n_{HCO_3} + n_{OH}$, ions/ml. × $10^{-14}$ | $\zeta$, mv |
|---|---|---|---|---|---|---|---|
| 0·2 | 115 | 3·011 | −115·2 | 0·6 | 255 | 9·111 | −127·5 |
| 0·25 | 125 | 3·778 | −113·7 | 0·7 | 317 | 10·64 | −134·7 |
| 0·3 | 130 | 4·544 | −111·0 | 0·8 | 380 | 12·16 | −140·5 |
| 0·4 | 156 | 6·072 | −112·9 | 0·9 | 444 | 13·69 | −145·4 |
| 0·5 | 197 | 7·598 | −119·0 | 1·0 | 510 | 15·21 | −150·0 |

The charge-determining ion at the silica–water interface is probably the bicarbonate ion, although in any calculation of the electrokinetic potential we must consider the possible contribution due to hydroxyl and carbonate ions. The calculation using Verwey and Overbeek's expression (" Theory of the Stability of Lyophobic Colloids," 1948, Elsevier Publ. Co. Inc., London), *viz.*,

$$\sigma = \left[\frac{2n\varepsilon kT}{\pi}\right]^{\frac{1}{2}} \sinh \frac{ze\zeta}{2kT}$$

(where $n$ = number of charge-determining ions of valency $z$ per ml., $\varepsilon$ = dielectric constant in the electrical double layer, $\boldsymbol{k}$ = Boltzmann's constant, $\boldsymbol{e}$ = electronic charge, $T$ = absolute temperature, $\zeta$ = electrokinetic potential) may not be strictly correct, since it was derived for a single electrolyte species. For a system containing a number of ions of mixed valencies the appropriate corresponding expression is

$$\sigma = \left[\frac{\varepsilon \boldsymbol{k} T}{2\pi}\right]^{\frac{1}{2}}[\Sigma n_i(\mathrm{e}^{-z_i F\zeta \boldsymbol{R}T} - 1)]^{\frac{1}{2}}$$

where $n_i$ is the number of ions, species $i$, of valency $z_i$, per ml.

The numbers of ions, $n_{\mathrm{H}}$, $n_{\mathrm{HCO_3}}$, $n_{\mathrm{OH}}$, $n_{\mathrm{CO_3}}$ in conductivity water may be calculated from the measured conductivity, the dissociation constants of carbonic acid, and the ionic product of water, if the conductivity is assumed to be due to these ions (Davies, *op. cit.*). Calculation on these lines shows that the contribution of the carbonate ion to the summation term in the above expression is negligible. The expression then reduces to Verwey and Overbeek's expression with $n = n_{\mathrm{H}} = n_{\mathrm{OH}} + n_{\mathrm{HCO_3}}$.

The electrokinetic potentials at the silica–water interface have therefore been calculated by using Verwey and Overbeek's expression and are shown plotted against the conductivity of the water in Fig. 2. The values of the charge, $\sigma$, used in these calculations were taken from the smoothed $\sigma$–$\kappa$ graph shown in Fig. 1.

It is noteworthy that these results indicate that the electrokinetic potential increases with increasing concentration of bicarbonate ion. This is contrary to the usual behaviour observed in aqueous electrolyte solutions, where the electrokinetic potential decreases with increasing concentration of the charge-determining ion. The usual tendency towards lower values of the potential at higher concentrations owing to the decrease in the thickness of the electrical double layer is outweighed in this case by the unusually rapid rate of increase of charge, due presumably to the operation of a high adsorption potential.

Wood (*J. Amer. Chem. Soc.*, 1946, **68**, 437) carried out many streaming-potential measurements at the silica–water interface. He found no systematic trend in the electrokinetic potentials with conductivity of the water and gave a value of −177 mv as the mean over the whole range of conductivity in which he worked. However, the variation of his results at ony one conductivity was often greater than the total variation in our figures over the whole range 0·2—1 gemmho.

Lachs and Biczyk (*Z. physikal. Chem.*, 1930, *A*, **148**, 441), using the streaming-potential method, report electrokinetic potentials at the silica–water interface as a function of the specific conductivity of the water ranging from −146 mv for water of conductivity 0·72 gemmho to −55 mv for water of conductivity 3 gemmho. The trend in the electrokinetic potential is in the reverse direction to that shown in our results, but it is doubtful if the impurities in the water used by Lachs and Biczyk were entirely carbonic acid, since conductivity water in equilibrium with a normal atmosphere rarely possesses a conductivity far in excess of 1 gemmho. Their results are, therefore, not comparable with the present measurements except perhaps in the case of their purest water (0·72 gemmho), where the difference is only a few mv.

Finally, we may conclude, from the agreement obtained between runs *A* and *B* (with water from a conventional still) on the one hand, and run *C* on the other, that water purified by the ion-exchange method is apparently free from undesirable surface-active impurities.

## EXPERIMENTAL

*Materials.*—Particle-sized specimens of fused silica powder were kindly provided by Mr. C. I. Dulin. Specimens were cleaned by boiling aqua regia and washed many times with conductivity water, the washings being removed after centrifugation. Later stages of washings were carried out with water of conductivity 0·25—0·4 gemmho.

Conductivity water was obtained for runs *A* and *B* from a still of the type described by Bourdillon (*J.*, 1913, **103**, 791) and modified by Bengough, Stuart, and Lee (*J.*, 1927, 2156). For run *C* the water was obtained by passing good distilled water through a column packed with resin, Biodemineralite, supplied by the Permutit Co.

*Sedimentation Experiments.*—These were carried out in a cylindrical cell, of 4-cm. diameter, graduated with a vertical scale in mm. Electrodes sealed into the bottom of the cell enabled the conductivity of the suspension to be determined by using an A.C. bridge. The cell was fitted with a ground-glass stopper at the top, which had, in turn, two subsidiary ground-glass stoppered inlets.

The silica specimen was washed into the cell, then allowed to settle, and the supernatant water poured off. A stream of nitrogen was then blown through the cell *via* a tube passing through one of the subsidiary inlets and reaching to the bottom of the cell. The tube was then removed, and the cell fitted directly to the tin receiver of the still (runs *A* and *B*) or to the delivery tube of the ion-exchange column (run *C*). The cell, thus filled with the purest conductivity water available, was clamped vertically in a thermostat at 25° ± 0·01°. The sedimentation velocity and the conductivity of the suspension were measured. A subsidiary stopper at the top of the cell was then removed for a short time, and the cell gently shaken. This contact of the water in the cell with the atmosphere caused the conductivity to increase. The sedimentation velocity and the conductivity were again measured. The procedure was repeated several times; each time the sedimentation velocity and the conductivity were measured.

The limiting velocity, $u_0$ was determined after adding concentrated hydrochloric acid to make an approximately N-solution. The mass of particles per ml. was determined by weighing the particles separated from a known volume of suspension. The density of the silica was determined in a density bottle, and the area per g. of the particles determined by the method of catalytic decomposition of hydrogen peroxide (Part I, *loc. cit.*).

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