741. *Determination of Electrokinetic Charge and Potential by the Sedimentation Method. Part VI.* Carborundum in Aqueous Solutions of Some Uni-univalent Electrolytes.*

By G. A. H. ELTON and J. W. MITCHELL.

Electrokinetic charges and potentials of carborundum surfaces in dilute aqueous solutions of various uni-univalent electrolytes are determined by the sedimentation method. The results are rather higher than those obtained by other workers, using the method of electro-osmosis. This is taken as confirmation of the theoretical prediction that the neglect of surface conductivity in the derivation of the Helmholtz–Smoluchowski equation for electro-osmosis may lead to considerable errors. The present results are used to obtain information concerning the relative magnitudes of the adsorption energies of some of the ions involved.

THIS paper gives the results of measurements by the sedimentation method (Elton, *Proc. Roy. Soc.*, 1949, *A*, **197**, 668; *J. Chem. Phys.*, 1951, **31**, 1317) of the electrokinetic charges and potentials of carborundum surfaces in dilute aqueous solutions of hydrochloric acid, nitric acid, potassium chloride, potassium nitrate, potassium hydroxide, and sodium chloride. Table 1 gives the values of the charge σ calculated as described previously (Dulin and Elton, Part I, *J.*, 1952, 286) from the measured velocities of sedimentation of homodisperse suspensions of carborundum powder in the solutions, and of ζ, the potential across the diffuse part of the double layer, obtained from σ in the usual manner (Dulin and Elton, *loc. cit.*; Part V, *loc. cit.*).

TABLE 1.*

	σ						ζ					
Concn. N	HCl	HNO_3	KCl	KNO_3	NaCl	KOH	HCl	HNO_3	KCl	KNO_3	NaCl	KOH
1×10^{-5}	505	420	590	450	565	435	113·7	104·9	122·0	104·8	119·9	106·7
2×10^{-5}	635	555	745	585	700	585	108·3	101·6	116·3	104·2	113·1	104·1
5×10^{-5}	900	775	1020	805	965	820	102·8	95·5	109·0	97·3	106·3	97·0
1×10^{-4}	1100	1000	1250	1040	1170	1065	95·5	90·9	101·9	92·8	98·6	89·7
2×10^{-4}	1365	1250	1505	1305	1440	1380	89·2	84·9	94·0	88·6	91·8	89·7
5×10^{-4}	1800	1730	1960	1880	1900	1820	80·5	77·7	84·5	82·5	83·0	80·5
1×10^{-3}	2260	2190	2420	2350	2360	2210	74·9	73·5	78·0	76·7	76·9	73·9
2×10^{-3}	2830	2750	3000	2940	2976	2620	69·3	68·0	72·0	71·1	71·5	65·9

* All the values of σ and ζ are negative.

Measurements of sedimentation velocity and conductivity were made in a cell of the type described by Benton and Elton (Part IV, *J.*, 1953, 2096). The results for potassium chloride were obtained by using two different homodisperse specimens of carborundum, in suspensions of widely differing particle concentration. The values of σ obtained from the two suspensions agreed to within 2% over the whole range of concentration, giving further

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* Part V, Dulin and Elton, *J.*, 1953, 2099.

confirmation of the soundness of the method, and indicating that in such suspensions (containing $6{\cdot}0 \times 10^{-5}$ g./ml. and $1{\cdot}2 \times 10^{-4}$ g./ml.) negligible particle–particle interaction occurs (see also Elton and Hirschler, Part II, *J.*, 1952, 2953; Dulin and Elton, 1953, *loc. cit.*). Results for the other electrolytes were obtained by using a single homodisperse specimen in each case.

In order to be able to assess the likely effect of variation in the quality (conductivity) of the water used in these experiments on the results obtained, σ was determined in water containing various amounts of carbonic acid. (The only significant impurity in good-quality conductivity water is dissolved carbon dioxide—see, *e.g.*, Davies, " Conductivity of Solutions," Chapman and Hall, London, 1933.) The potential was calculated from σ in the same manner as for uni-univalent electrolytes, the small number of carbonate ions present having no significant effect on the potential (Benton and Elton, *loc. cit.*). The results obtained are shown in Table 2, the charge and potential being recorded as functions of κ, the conductivity of the water. It is seen that σ increases with κ, while ζ is approximately constant over a considerable range. The water used as solvent in the experiments on the various electrolytes (except potassium hydroxide, see below) was " equilibrium " water of conductivity around 1 gemmho, depending on atmospheric conditions. Variation of $\pm 0{\cdot}2$ gemmho in the conductivity of the solvent will cause a variation of approximately ± 50 e.s.u. in the charge carried by carborundum in the solvent, but the error introduced into the results for σ for the electrolyte solutions will probably be considerably less than this as the " solvent charge " is not additive to the " solute charge " (see p. 3692). In fact, experiments carried out on different days, using a given electrolyte dissolved in two specimens of water differing in conductivity by up to 0·2 gemmho, gave results for σ in agreement to within 20 e.s.u. over the whole concentration range.

TABLE 2.

κ, gemmho	0·2	0·4	0·6	0·8	1·0	1·5	2·0
σ, e.s.u.	169	243	360	421	473	553	570
ζ, mv	129·5	143·0	146·5	147·6	148·7	143·9	137·7

All the above values are negative.

Discussion.—Few electrokinetic data for carborundum are available for comparison with this work. Fairbrother and Mastin (*J.*, 1924, **125**, 2319; 1925, **127**, 332) studied, *inter alia*, the electrokinetic potential of carborundum in hydrochloric acid and potassium chloride solutions, using the method of electro-osmosis through a plug of carborundum. In calculating ζ from their measurements, they used the simple Helmholtz–Smoluchowski electro-osmosis equation $V = \zeta\varepsilon E/(4\pi\eta)$, where V is the velocity of electro-osmosis under a potential gradient E, and ε and η are respectively the dielectric constant and the viscosity in the double layer, taken as equal to the bulk values. However, as pointed out by Overbeek and Wijga (*Rec. Trav. chim.*, 1946, **65**, 556), application of this equation to results obtained from measurements of electro-osmosis through plugs is likely to lead to erroneous values of ζ, since it makes no allowance for the effect of surface conductance. Table 3 gives a comparison of our results for ζ in hydrochloric acid and potassium chloride solutions with Fairbrother and Mastin's at suitably interpolated concentrations. It is seen that the values of ζ in potassium chloride solution from electro-osmosis are about 30% lower than from sedimentation velocity over the entire concentration range, while for hydrochloric acid the values from electro-osmosis are about 40% lower in the most dilute solutions, and the difference increases steadily to 70% in the most concentrated solutions. It would appear likely from this that the effect of surface conductance on the electro-osmosis is considerable, and is relatively greater in hydrochloric acid than in potassium chloride solutions, especially at the higher concentrations.

TABLE 3.

Concentration, N ...	2×10^{-5}	5×10^{-5}	1×10^{-4}	2×10^{-4}	5×10^{-4}	1×10^{-3}	2×10^{-3}
$\frac{\zeta_{\text{electro-osmosis}}}{\zeta_{\text{sedimentation}}}$ HCl	0·554	0·496	0·461	0·421	0·385	0·334	0·289
KCl	0·628	0·624	0·648	0·670	0·710	0·718	0·694

Elton (1949, *loc. cit.*) studied the effect of electroviscosity on the velocity of sedimentation of carborundum particles in potassium chloride solutions, before the theory for non-spherical particles had been adequately developed. In order to estimate the order of the electrokinetic potentials, he assumed that the carborundum particles could be treated as spheres, and used a simple expression for the electroviscosity which, as he pointed out, will lead to high values for ζ. His values are, in fact, roughly twice those obtained by using the full expression for non-spherical particles.

It is seen from Table 1 that the charges in potassium chloride and sodium chloride solutions differ only very slightly over the whole range, those in potassium chloride solution being slightly the larger. This indicates that the potassium and the sodium ion possess similar adsorption energies at the carborundum surfaces, that for the potassium ion being slightly the smaller (*i.e.*, more negative). This has been confirmed by measurements of ion adsorption (Elton and Mitchell, unpublished work), the values being $-7{\cdot}3$ kcal. for the potassium ion, and $-7{\cdot}2$ kcal. for the sodium ion, for adsorption from 10^{-3}N-solutions.

The charge in hydrochloric acid is about 100 e.s.u. less than that in potassium chloride solutions at the lowest condentrations studied, and the difference rises slightly with increasing concentration. This is probably due, at least in part, to the fact that in the acid solution the dissociation of ions originally present in the conductivity water is suppressed by addition of acid, and their contribution to the total charge is lost. It is seen from Table 2 that the charge in the pure solvent (" equilibrium " water, $\kappa \simeq 1$ gemmho) is about 400 e.s.u., so we must conclude that the contribution of the " solvent charge " is not additive to the " solute charge " in the salt solution—owing to the fact that addition of solute alters the potential in the adsorbed layer (see also Dulin and Elton, 1953, *loc. cit.*). The charge in nitric acid is also less than that in potassium nitrate solutions, the difference being about 30 e.s.u. at the lowest, and about 200 e.s.u. at the highest, concentrations.

The charges in nitric acid are consistently lower than those in hydrochloric acid, the difference being 80—125 e.s.u. over the concentration range 1×10^{-5}N to 2×10^{-3}N. The charges in potassium nitrate solutions are consistently lower than those in potassium chloride solutions, the difference being 60—215 e.s.u. over this concentration range. These differences indicate that the adsorption energy of the nitrate ion at a carborundum surface is appreciably less (*i.e.*, more negative) than that of the chloride ion. This has been confirmed by measurements of ion adsorption (Elton and Mitchell, *loc. cit.*), the values for adsorption from a 10^{-3}N-solution being $-4{\cdot}0$ kcal. for the nitrate ion, and $-3{\cdot}8$ kcal. for the chloride ion.

The results for potassium hydroxide solutions were obtained in water of very low carbon dioxide content ($\kappa \simeq 0{\cdot}2$ gemmho) in order to avoid the complication of considerable reaction of the hydroxyl ion with bicarbonate ions from the solvent. There will therefore be an unusually small " solvent charge " in this case. The charges in potassium hydroxide solutions are very similar to those in potassium nitrate solutions, especially at the lower concentrations, so we may draw the qualitative conclusion that the adsorption energy of the hydroxyl ion at a carborundum surface is, at these concentrations, not very different from that of the nitrate ion.

EXPERIMENTAL

Materials.—Carborundum powder (700 mesh) was supplied by the Carborundum Company Ltd. It was cleaned by treatment with alcohol–nitric acid, followed by boiling aqua regia, and washed many times with conductivity water. Purification of the solutes used has been described previously (Parts I, III, and V, *locc. cit.*), except that for potassium hydroxide " AnalaR " pellets were washed with conductivity water to remove surface carbonate, and a solution made up in good-quality conductivity water ($\kappa \simeq 0{\cdot}2$ gemmho), and kept in a waxed bottle under nitrogen. The solution was standardised against potassium hydrogen phthalate, and used immediately.

Particle-sizing of Carborundum.—This was done as described in Part I. Specimens of two particle sizes were used, with limiting sedimentation velocities (u_0) of $3{\cdot}94 \times 10^{-3}$ and $5{\cdot}32 \times 10^{-3}$ cm./sec. The areas per g. (A_0) of the particles, determined as described in Part I (*loc. cit.*), were $6{\cdot}23 \times 10^4$ and $3{\cdot}85 \times 10^4$ cm.^{2}, respectively.

Sedimentation Experiments.—These were carried out in a cell of the type described in Part IV (*loc. cit.*). The cell, containing the carborundum and about 180 ml. of conductivity water, was clamped vertically in a thermostat at 25·00° ± 0·01°. Additions of electrolyte stock solution were made with a microburette, and the conductivity of the solutions obtained was measured on a conventional A.C. bridge, the concentrations being calculated from the measured conductivities. The weight of particles per ml. of the suspension (M) was determined before each run by taking 25 ml. of the original suspension in conductivity water, centrifuging out the particles, and drying and weighing them on a microbalance. (In this work M was usually between 4×10^{-5} and 4×10^{-4} g./ml.) As the volume of the suspension was changed during the run by addition of electrolyte solution, a slightly different value of M has to be used at each concentration. This technique was used in preference to the method of successive dilution in order to avoid loss of a slight film of particles which tended to cling to the surface of the solution.

BATTERSEA POLYTECHNIC, S.W.11.

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