429. *Determination of Electrokinetic Charge and Potential by the Sedimentation Method. Part V.* Silica in Some Aqueous Nitrate Solutions.*

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Electrokinetic charges and potentials of fused silica surfaces in dilute aqueous solutions of various nitrates are determined by the sedimentation method. For univalent cations, the results for nitrates are close to those for the corresponding chlorides, confirming that the adsorption energies of the nitrate and chloride ions are similar, but for higher-valency cations there is an increasing tendency towards higher charges in the nitrate solutions. Possible causes of this effect are discussed.

THIS paper gives the results of measurements by the sedimentation method of the electrokinetic charges and potentials of fused silica surfaces in dilute aqueous solutions of potassium, barium, lanthanum, and thorium nitrates, and of nitric acid. Results for the corresponding chloride solutions were reported in Parts I and III (Dulin and Elton, *J.*, 1952, 286; 1953, 1168). The Table gives the values of the charge, σ, calculated as described previously from the measured sedimentation velocities of homodisperse suspensions of fused silica powder in the nitrate solutions. In the case of lanthanum and thorium nitrates, increase of concentration from zero brings about reversal of the initial negative charge, owing to ready adsorption of the high-valency cation (and hydrolysis products) into the fixed part of the double layer. In the region of the isoelectric point, the values given in the Table are of lower accuracy than usual, since the measured sedimentation velocity, u, is very near to the limiting velocity, u_0, and fairly small errors in the determination of either of these velocities result in relatively large errors in the values of $(u_0 - u)$, required in the calculation of σ. Calculation of ζ, the potential across the diffuse part of the double layer, from σ is straightforward for uni-univalent electrolytes, but is more complicated for solutions containing high-valency ions, especially when hydrolysis is considerable, as, *e.g.*, with thorium nitrate solutions. The hydrolysis

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* Part IV, preceding paper.

correction in the calculation of ζ, for the case of cation hydrolysis, is more important when the charge is negative, *i.e.*, when the hydrolysed ion is acting as a counter-ion (see Dulin and Elton, 1953, *loc. cit.*). For thorium nitrate, this occurs only below 2 × 10^{-5}N, but for lanthanum nitrate the charge is negative at all concentrations below 5 × 10^{-4}N, and hydrolysis corrections have to be applied as described previously. Although, for convenient reference, both charges and potentials are given in the Table, the results are discussed below solely in terms of the charges, in view of the uncertainties inherent in the calculation of the potentials.

	σ, e.s.u./cm.^{2}					ζ, mv				
c, N	HNO_3	KNO_3	$Ba(NO_3)_2$	$La(NO_3)_3$	$Th(NO_3)_4$	HNO_3	KNO_3	$Ba(NO_3)_2$	$La(NO_3)_3$	$Th(NO_3)_4$
1 × 10^{-3}	3770	4207	1369	1718 *	4928 *	99·5	105·0	34·5	66·1 *	114·0 *
5 × 10^{-4}	3107	3391	1413	0	2883 *	107·2	112·4	43·1	0	104·9 *
2 × 10^{-4}	2228	2491	1355	496	1368 *	113·5	118·4	53·2	23·6	91·4 *
1 × 10^{-4}	1772	1991	1201	643	744 *	119·4	125·3	58·8	32·4	80·3 *
5 × 10^{-5}	1418	1570	1001	633	368 *	125·7	130·9	63·0	36·0	60·4 *
2 × 10^{-5}	1013	1187	856	532	0	132·0	140·0	70·7	44·4	0
1 × 10^{-5}	822	1017	750	487	160	138·5	149·8	76·1	49·3	23·3
5 × 10^{-6}	—	—	713	484	202	—	—	83·7	55·2	30·8
2 × 10^{-6}	—	—	678	452	370	—	—	94·2	59·0	43·8
1 × 10^{-6}	—	—	691	—	527	—	—	103·8	—	53·0

All values are negative except those marked *.

Discussion.—The charge in nitric acid solutions is always lower than in potassium nitrate solutions of the same concentration, the difference being about 200 e.s.u. at 1 × 10^{-5}N, rising steadily to about 700 e.s.u. at 2 × 10^{-3}N. Similar differences were found between the results for hydrochloric acid and potassium chloride, and were ascribed to the stripping off in acid solutions of the charge due to ions from the solvent. The charges in nitric acid are close to those in hydrochloric acid, the differences over most of the range being less than 5%. There is a slight trend in the differences, the charge for nitric acid being rather lower in the most dilute solutions, and higher in the more concentrated solutions. The similarity between the two sets of results indicates that the energy of adsorption of the nitrate ion on to a fused silica surface cannot differ greatly from that of the chloride ion. This deduction has been confirmed by Benton and Elton (*Trans. Faraday Soc.*, 1953, in the press), quantitative experiments giving values of —2·48 kcal. for the nitrate ion, and —2·44 kcal. for the chloride ion, for adsorption from 10^{-4}N-solutions. The results for potassium nitrate are almost identical with those for potassium chloride at 10^{-3}N, but show a slight but definite trend towards lower relative values as the concentration decreases, a parallel trend to that mentioned above for nitric acid.

Barium nitrate differs appreciably from barium chloride, the charges over the range 10^{-6}—10^{-4}N being about 100 e.s.u. higher. Over the range 10^{-4}—10^{-3}N the difference rises to almost 500 e.s.u. The accuracy in the latter range is rather low, errors of the order of 100 e.s.u. being possible owing to low values of $(u_0 - u)$. Although the adsorption energies of the nitrate and chloride ions have been shown to be nearly the same, a higher negative charge may be obtained for the nitrate solutions for the following reason. It is known that in solutions of nitrates of bivalent cations, the tendency to form ion-pairs is much greater than in solutions of the corresponding chlorides (see, *e.g.*, Robinson, *ibid.*, 1940, **36**, 735, 1135; Robinson and Stokes, *ibid.*, p. 1137). Since a singly charged ion-pair will be less strongly attracted to the negatively charged surface than a doubly charged cation, a larger negative charge will be obtained, provided that the ion-pair does not possess an abnormally high adsorption energy.

A rather similar effect may occur in lanthanum nitrate solutions. In the most dilute solutions, a negative charge almost equal to that in lanthanum chloride solutions is obtained, but at concentrations just below the isoelectric point, 5 × 10^{-4}N, the nitrate charge is rather more negative than the chloride charge. On the positive side of the iso-electric point the nitrate charge is more positive than the chloride charge, possibly owing to the low electrostatic repulsion by the surface of ion-pairs from the nitrate solution. In this case, however, hydrolysis is a complicating factor.

Thorium nitrate is strongly hydrolysed, and the large number of ionic species in the solutions renders analysis of the results difficult, since each species possesses its own characteristic adsorption energy. The charge in the most dilute nitrate solutions is considerably more negative than in the corresponding chloride solutions, the isoelectric point being 2×10^{-5}N, compared with 4×10^{-6}N. On the positive side of the isoelectric point, the nitrate charge increases rapidly, and has become more positive than the chloride charge by 10^{-3}N, indicating strong adsorption of a positively charged species from the nitrate solutions.

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