968. *The Adsorption of Cations at the Silver Iodide–Solution Interface. Part I. Lanthanum and Neodymium.*

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The adsorption of the cations of lanthanum and neodymium on powdered silver iodide has been measured, by use of a radiotracer method, at a constant concentration of the potential-determining iodide ion, as a function of pH. In all cases, plots of log moles of cation adsorbed against log moles of the equilibrium concentration of cation were linear at the lower concentrations. The adsorption behaviour of neodymium was virtually independent of pH in the region 1·9—6·0. In the case of lanthanum the adsorption appeared to be independent of pH in the region 2·0—5·0, but there was a marked increase above 6·5, which was ascribed to the increased adsorption of the hydrolysed lanthanum ion.

The effects of tervalent cations on the stability of sols and suspensions have played an important part in the development of theories of the coagulation process. In general, however, present theories of colloid stability [1,2] are based only on the interaction of the

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[1] Derjaguin and Landau, *Acta Physicochim.*, 1941, **14**, 633.

[2] Verwey and Overbeek, "Theory of Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.

diffuse double-layers of the particles, and the specific effects of the coagulating ions are not taken into account. Experimentally, specific-ion effects are evident from several viewpoints, one of the simplest being the variation of the coagulation concentration with the nature of the ion, for ions of the same valency.[3,4] Moreover, the concentration at which coagulation occurs can be considerably influenced by hydrolysis of the coagulating ion.[5-8] For a more refined interpretation of coagulation mechanisms and the nature of the electrokinetic potential, measurements of ion adsorption are required. The availability of radiotracer techniques now renders such measurements possible in dilute solution. Previously, analytical techniques were not sufficiently sensitive for direct measurement of the small differences in concentration involved.

In the present study the adsorption of lanthanum and neodymium ions on silver iodide has been investigated at different pH values as a function of concentration, over a range of concentrations above and below that at which the coagulation of silver iodide sols normally occurs. Complementary measurements have also been made of the electrokinetic properties of the particles over the same range.

EXPERIMENTAL

Materials.—Distilled water was passed through a mixed-bed ion-exchange resin and redistilled in an all-Pyrex apparatus. Silver nitrate, sodium nitrate, and potassium iodide were AnalaR grade. Lanthanum nitrate was B.D.H. material. Neodymium nitrate was prepared by dissolving Nd_2O_3 (Johnson Matthey) in nitric aid and recrystallizing the nitrate several times from distilled water. The concentration of the lanthanum nitrate and neodymium nitrate solutions was determined by titration with standard lead nitrate solutions in the presence of EDTA and hexamine, with Xylenol Orange as indicator.

Radioactive Materials.—Lanthanum-140 and neodymium-147 were obtained from the Radiochemical Centre, Amersham, as solutions of their nitrates. The solutions were assayed before leaving Amersham, and stock solutions (*ca.* 10^{-5}M) were prepared from these by dilution. The lanthanum and neodymium concentrations in the stock solutions were determined volumetrically (as above). The half-lives of both isotopes were determined. For ^{140}La a value of 45·2 hr. was obtained, in reasonable agreement with the literature values. With neodymium there was evidence of the presence of some short-lived isotopes, but after a short time the value was 11·6 days. Most experiments were carried out after the initial decay had occurred, and there was no evidence to suggest that these or ^{147}Pm, daughter of ^{147}Nd and a low-energy β-emitter with a half-life of 2·6 years, interfered with the determination of neodymium adsorption.

Silver Iodide Powder.—Silver iodide was precipitated by mixing 0·2N-silver nitrate and 0·2N-potassium iodide in equal volumes with vigorous stirring. The precipitated material was washed thoroughly with distilled water and aged at 90° for 12 hr. A number of samples thus prepared were combined and washed with conductivity water until the conductivity of the supernatant was close to that of conductivity water. The precipitate was dried at 70°, ground with an all-glass pestle and mortar, and sieved through a Nylon mesh to remove the larger particles. The surface area of the sample was determined from argon adsorption, krypton adsorption, double-layer capacity measurements, and photomicrography.[9] The mean value was 0·7 m.^{2}/g.

Adsorption Measurements.—A solution (1 ml.) containing 10^{-3}M-potassium iodide and 10^{-2}M-sodium nitrate was added to a glass-stoppered Pyrex test-tube of *ca.* 20 ml. capacity. An aliquot part of an inactive neodymium or lanthanum nitrate solution was then added and the total volume adjusted to 8 ml. The radioactive solution (1 ml.) of the cation was then added, and the pH adjusted by the addition of nitric acid or sodium hydroxide solution. The volume

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[3] Kruyt, " Colloid Science," Vol. 1, Elsevier, Amsterdam, 1952.
[4] Težak, Matijević, and Schulz, *J. Phys. Chem.*, 1955, **59**, 76.
[5] Matijević, Abramson, Schulz, and Kerker, *J. Phys. Chem.*, 1960, **64**, 1157.
[6] Matijević, Mathai, Ottewill, and Kerker, *J. Phys. Chem.*, 1961, **65**, 826.
[7] Packham, *J. Appl. Chem.*, 1962, **12**, 556, 564.
[8] Matijević, Couch, and Kerker, *J. Phys. Chem.*, 1962, **66**, 111.
[9] Jaycock, Ottewill, and Rastogi, 3rd Internat. Congr. Surface Activity, 1960, p. 283.

of acid or alkali was recorded, and sufficient distilled water added to bring the total volume to 10 ml. The tubes were shaken mechanically at room temperature for 60—90 min., a sample (2 ml.) was removed and evaporated to dryness, and the counts per min. were determined. Since the concentration of the initial solution had been estimated analytically, and its activity determined, the adsorption of the tervalent ion on the glass was obtained by simple proportionation, with allowance for the decay of the isotope with time. Isotherms for the adsorption of the tervalent ions on the glass tubes were obtained at each pH used.

Silver iodide powder (0·2 g.) was added to the remaining 8 ml. of liquid. The tubes were shaken mechanically for 1 hr. and set aside for 15—18 hr. A further shaking for 1 hr. was followed by centrifugation, of the whole tube, for 5 min. at 2500 r.p.m. A sample (2 ml.) of the supernatant was removed and evaporated to dryness, and the activity determined. From the latter count the concentration of tervalent ion in the supernatant (equilibrium concentration) was calculated. The difference between this concentration and the initial concentration with allowance for volume changes, gave the amount adsorbed by the glass and the silver iodide. Subtraction of the amount adsorbed on the glass corresponding to this equilibrium concentration gave the amount adsorbed on the silver iodide powder.

Although this procedure proved accurate in the intermediate concentration regions (10^{-5}—10^{-3}M) it was not sufficiently precise at lower or higher concentrations or in regions where hydrolysis of the ions increased the extent of adsorption. In these regions it was more precise to determine the adsorption from the activity of the powder. Hence, the silver iodide powder, which remained in the bottom of the tube after decantation of the supernatant, was washed with 3 ml. of 10^{-3}M-NaNO$_3$ + 10^{-4}M-KI solution, and the washings removed. The powder was then agitated with a small volume of water (*ca.* 1 ml.), transferred as quantitatively as possible as a slurry to a counting cup, evaporated to dryness, and the count determined. Although this procedure appeared arbitrary it gave satisfactory results. Evaporation of the slurry without washing gave high counts because radioactive liquid was trapped by the powder. A small amount of activity was removed in the first washing and virtually none after this provided that the washing was carried out quickly with cold distilled water at, or near, neutral pH. On protracted standing, *e.g.*, 24 hr., some desorption occurred; this could be accelerated by reducing the pH to 2 or lower. The activity of the washings was always checked. The agreement obtained between the amounts adsorbed determined from supernatant counts and powder counts in this and earlier work [10] suggested that the technique was reliable and that self-absorption in the thin powder layers used for counting was negligible.

Adsorption equilibrium with the powder was obtained within 1—2 hr. (more rapidly with the glass), and after this no further changes were observed except at high pH where precipitation of the metal hydroxide occurred. Results are not reported in this Paper for this region.

The accuracy of the adsorption results was ±5% in the equilibrium concentration region 10^{-6}—10^{-5}M, and ±3% above this. All measurements, unless otherwise stated, were made at room temperature, 20 ± 1°

Radioactive material was counted with a Philips Geiger–Muller tube, type 18505, with a mica window 1·5—2·0 mg./cm.^{2} thick. The geometry was kept constant for all counts. Glass cups of 5 ml. capacity were used for counting since they allowed transfer of a greater volume of the liquid with the powder than did the normal planchettes. The water was removed in all cases by evaporation under an infrared lamp.

Microelectrophoresis Experiments.—The solutions were set up in the same manner as in the adsorption experiments except that 20 ml. of solution was taken and the radiotracer was omitted. A small quantity (<5 mg.) of powder was added to the solution, and after shaking it was allowed to stand for *ca.* 18 hr. It was calculated that the amount of solid added was not sufficient to affect the concentration, and hence the concentration was taken to be the equilibrium one. Just prior to measurements the suspension was treated ultrasonically for 1—2 min. to obtain a good dispersion.

Mobility determinations were carried out in an apparatus similar to that described by Alexander and Saggers [11] but fitted with a slit ultramicroscope. The cell was of the Mattson type.[12] Zeta-potentials were calculated using the formulae of Overbeek.[13]

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[10] Matijević, Abramson, Ottewill, Schulz, and Kerker, *J. Phys. Chem.*, 1961, **65**, 1724.
[11] Alexander and Saggers, *J. Sci. Instr.*, 1948, **25**, 374.
[12] Mattson, *J. Phys. Chem.*, 1928, **32**, 1532; 1933, **37**, 223.
[13] Overbeek, *Kolloid-Beih.*, 1943, **54**, 287.

RESULTS

Neodymium.—The results for the adsorption of neodymium on silver iodide powder at pI 4 in 10^{-3}M-sodium nitrate are presented in Fig. 1. At the lower neodymium concentrations a reasonably linear plot was obtained when log moles of neodymium adsorbed per gram of silver iodide was plotted against log molar equilibrium concentration of neodymium nitrate. This indicated that an adsorption isotherm of the Freundlich type was obeyed, namely, $\log x = \log k + (1/n) \log c$ where x = moles of neodymium adsorbed per gram of silver iodide, c = equilibrium concentration of cation, and k and n are constants. The curves were identical over the pH range 1·9—6·0. At the higher concentrations of neodymium the curves showed an upward rise in the amount adsorbed with increase in the neodymium concentration and the points suggest that this effect is greater at pH 6·0 than at 1·9.

The zeta-potential of the suspension was also investigated as a function of the neodymium concentration at pH values of 2·6 and 5·8, and as a function of pH in 10^{-4}M-neodymium nitrate. The ionic environment was the same as that used in the determination of the adsorption isotherm in order to facilitate a comparison between adsorption and electrokinetic data. The results obtained as a function of neodymium concentration at pH values of 2·6 and 5·8 are given in Fig. 3; within the limits of experimental error the two sets of results could not be distinguished. The curve obtained in 10^{-4}M-neodymium nitrate, as a function of pH (Fig. 3a), showed that the particles reversed their charge in the pH region 6·25—8·25 and became positively charged. This effect was attributed to the onset of hydrolysis of the neodymium ion in this pH region (see later).

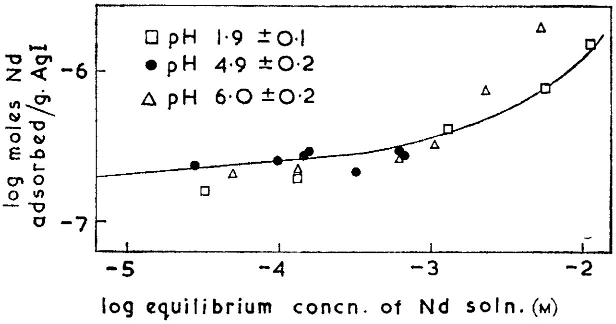

FIG. 1. Variation of neodymium adsorbed with equilibrium concentration of neodymium nitrate, in a solution 10^{-3}M in $NaNO_3$ and 10^{-4}M in KI (pH adjusted with nitric acid).

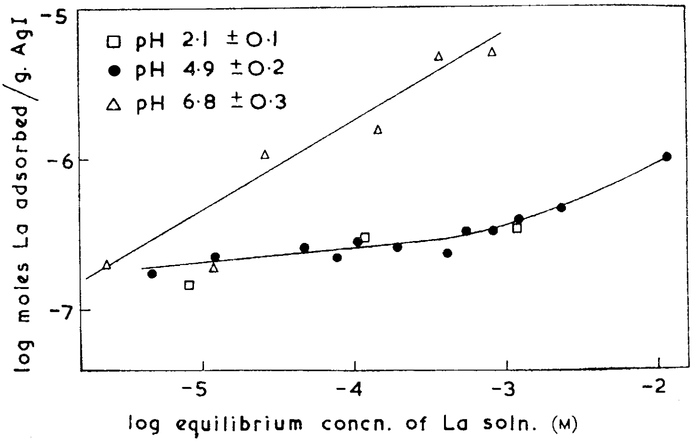

FIG. 2. Variation of lanthanum adsorbed with equilibrium concentration of lanthanum nitrate, in a solution 10^{-3}M in $NaNO_3$ and 10^{-4}M in KI (pH adjusted with nitric acid).

Lanthanum.—The adsorption isotherms obtained for the lanthanum ion on silver iodide are presented in logarithmic form in Fig. 2. The results obtained at pH 2·1 and 4·9 were indistinguishable, and close to those obtained with neodymium. The results obtained at pH 6·8, however, revealed a considerable increase in the extent of adsorption.

The curves of zeta-potential against log concentration of lanthanum are also given in Fig. 3. The results obtained at pH values of 2·6 and 5·6 fell, within experimental limits, on the same curve and were very close to those obtained with neodymium. Examination of the particles in 10^{-4}M-lanthanum nitrate, as a function of pH, showed that the particles became positively charged in the region 6·25—8·25. This was so if measurements were made within 1 hr. of adjusting the pH to the higher value. On standing overnight in this region, however, the particles tended to become negatively charged again.

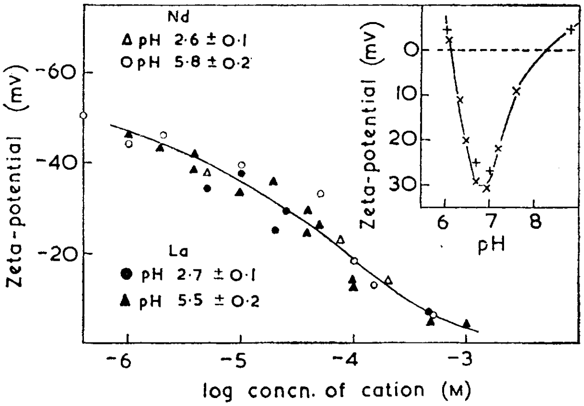

FIG. 3. Variation of zeta-potential with concentration of neodymium or lanthanum nitrate solution, 10^{-3}M in NaNO$_3$ and 10^{-4}M in KI.
(Inset: Variation of zeta-potential with pH. X, in 10^{-4}M-neodymium nitrate; +, in 10^{-4}M-lanthanum nitrate.)

DISCUSSION

Adsorption.—In the classical work on silver iodide it is assumed that the potential at the interface is largely determined by the adsorption of the potential-determining silver or iodide ions. Thus, at pI 4, the condition employed in the present work, the surface-charge density on the solid can be attributed to an excess of iodide ions in the lattice. The charge in the electrolyte solution can be divided into two layers, the Stern layer [14] and the diffuse double layer.[15,16] The adsorption excess of the cations at the interface can therefore be divided into $\Gamma_{C^{v+}}{}^{S}$ in g.-ions per cm.^{2} for cations adsorbed in the Stern plane and $\Gamma_{C^{v+}}{}^{D}$ for cations adsorbed in the diffuse double-layer, where v = the valency of the ion. Thus, for the total cation adsorption, Γ^+, we can write

$$\Gamma^+ = \Gamma_{C^{v+}}{}^{S} + \Gamma_{C^{v+}}{}^{D}$$

Similarly, for anion adsorption,

$$\Gamma^- = \Gamma_{A^{v-}}{}^{S} + \Gamma_{A^{v-}}{}^{D}$$

Hence, the surface-charge density, σ, on the solid will be compensated by the adsorption excesses of the ions in solution. Hence,

$$\sigma = e(v^+ \Gamma^+ - v^- \Gamma^-)$$

Under the conditions used in the present work the counter-ions were initially sodium

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[14] Stern, *Z. Elektrochem.*, 1924, **30**, 568.
[15] Gouy, *J. phys.*, 1910, **9**, 457; *Ann. Physik*, 1917, **7**, 129.
[16] Chapman, *Phil. Mag.*, 1913, **25**, 475.

and potassium. On addition of the tervalent cation, ion-exchange occurs in both layers to an extent which depends on the ratio of the concentrations of univalent to tervalent ion; Herak and Mirnik[17] Found that equivalent exchange appears to occur. Thus, formally, one can write

$$\Gamma^{+} = \Gamma_{C^{+}}{}^{S} + \Gamma_{C^{+}}{}^{D} + (\Gamma_{C^{3+}}{}^{S} + \Gamma_{C^{3+}}{}^{D})$$

where the two terms in parentheses represent the total adsorption of the tervalent cation. In terms of double-layer theory the principal difficulty is to determine whether the latter is measured by experiment.

In view of the low level of adsorption, the extent of adsorption was determined experimentally from the radioactivity of the powder after washing and drying. Washing of the powder was necessary to remove radioactive liquid trapped between the particles after the first decantation. During the washing some of the readily exchangeable cations in the diffuse double layer ($\Gamma_{C^{3+}}{}^{D}$) will be washed away. Those remaining on the surface will consist of cations strongly adsorbed, together with some from the diffuse layer.

The small amount of rapid desorption of cation followed by an extremely slow desorption process suggested that most of the ions were strongly adsorbed on the surface. The nature of the ion adsorbed on the surface is not made clear from the experiments, however, since these only measured the uptake of neodymium or lanthanum. It is not inconceivable that hydrolysis products are always present in solution and that these become adsorbed rather than the simple cations.

The increase in the adsorption of lanthanum, and the reversal of charge of the particles in 10^{-4}M-lanthanum nitrate and 10^{-4}M-neodymium nitrate, occurs in the pH region in which hydrolysis of the cation starts to become appreciable, and is in accord with some previous observations and subsequent work of the authors,[18] that increased adsorption of ions occurs with the onset of hydrolysis. According to Biedermann and Ciavatta[19] the first hydrolysis reaction of lanthanum appears to be

$$\mathrm{La^{3+} + H_2O = La\,OH^{2+} + H^{+}}$$

with an equilibrium constant of $10^{-10\cdot1}$. Hence it appears that the hydrolysis of lanthanum is small below pH 6 but becomes appreciable as 7 is approached and leads to different adsorption characteristics for the hydrolysed ion.

The hydrolysis of the neodymium ion has been investigated by Moeller[20] who suggested that $\mathrm{Nd\,OH^{2+}}$ was formed. The degree of hydrolysis increased with decrease in cation radius in the series La to Y. Although, on this basis, the neodymium ion is more hydrolysable than the lanthanum ion, the differences appear to be small.

It is not inconceivable, however, that the increase in adsorption of neodymium at pH 1·9 and 6·0, at the higher neodymium nitrate concentration, is also due to the gradual increase in hydrolysed material in solution as the cation concentration is increased.

Comparison between Electrokinetic Experiments and Adsorption.—The electrokinetic surface-charge density, σ_2, of the silver iodide, as a function of neodymium nitrate concentration, at pH 2·6, was calculated from the expression[2]

$$\sigma_2 = \pm\left[\frac{NkT\varepsilon}{2\pi}\sum\frac{c_{\pm}}{v_{\pm}}\left(\exp\frac{-v_{\pm}e\zeta}{kT} - 1\right)\right]^{\frac{1}{2}}$$

where $c_{\pm}$ = concentration of the ions in g.-equiv./ml. and $v_{\pm}$ = the valency of the ion. Allowance was made for the sign of both the zeta-potential and the valency.

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[17] Herak and Mirnik, *Kolloid-Z.*, 1961, **179**, 130; 1960, **168**, 139.

[18] Abramson, Jaycock, and Ottewill, following Paper.

[19] Biedermann and Ciavatta, *Acta Chem. Scand.*, 1961, **15**, 1347.

[20] Moeller, *J. Phys. Chem.*, 1946, **50**, 242.

As the ionic strength remained virtually constant during the electrophoresis experiments the change in electrokinetic surface-charge density due to the adsorption of the neodymium ion can be written

$$\Delta\sigma_2 = \sigma_2{}^0 - \sigma_2$$

where $\sigma_2{}^0$ = electrokinetic surface-charge density in the absence of neodymium, and σ_2 = the electrokinetic surface-charge density at a specified neodymium concentration. A plot of $\Delta\sigma_2$ against concentration of neodymium is given in Fig. 4.

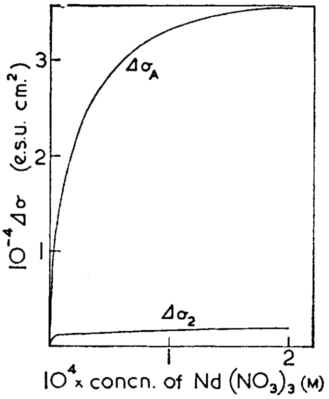

FIG. 4. Variation of $\Delta\sigma_A$ and $\Delta\sigma_2$ with concentration of neodymium nitrate.

For the purpose of comparison the amount of neodymium adsorbed has been converted into a surface-charge density by means of the relationship, $\Delta\sigma_A = 3xe$. In Fig. 4, $\Delta\sigma_2$ and $\Delta\sigma_A$ are plotted against the molar concentration of neodymium. The comparison suggests that a large part of the material adsorbed is on the surface side of the slipping plane or that $\Delta\sigma_A$ is overestimated by the use of too high a valency for the adsorbed species. The fact that the net electrokinetic surface-charge density remains negative suggests either that anions are also adsorbed behind the slipping plane or that the neodymium was adsorbed in a virtually electroneutral form. The incorporation of anions into the Inner Helmholtz Layer, on a negatively charged surface, was suggested by Grahame[21] and is supported by the work of Bockris, Devanathan, and Muller.[22] Benton, Elton, and Harrison[23] also suggested that simultaneous anion and cation adsorption may occur on the basis of electrokinetic experiments. In systems such as those used in the present work the use of electrokinetic measurements to determine the extent of ion adsorption is clearly invalid since the zeta-potential only reflects the net change in the surface-charge density at the slipping plane.

However, the problem is also posed as to why the products of ion hydrolysis reverse the charge more readily than " simple " ions. The evidence presented in this and the following Paper indicates that a considerable increase in the extent of adsorption occurs once hydrolysis of the ion commences. It appears probable that once hydrolysis has commenced some polynuclear complexes are formed and these are preferentially adsorbed. Under these conditions the plane of shear may come into closer coincidence with the surface of the adsorbed polynuclear complex layer.

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[21] Grahame, *Chem. Rev.*, 1947, **41**, 441.
[22] Bockris, Devanathan, and Muller, *Proc. Roy. Soc.*, 1963, *A*, **274**, 55.
[23] Benton, Elton, and Harrison, *J.*, 1960, 4019.