974. *Sorption from Dilute Aqueous Electrolyte Solutions by Zirconia.*

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The extent of sorption by zirconia from dilute aqueous solutions of sodium chloride and hydrochloric and nitric acid, and a number of mixtures of these electrolytes, has been studied by conductometric and potentiometric measurement of concentration loss from solution. Sorption of sodium ion was not detected from neutral or acid solutions. Sorption from nitric acid is rather less in extent than from hydrochloric acid at corresponding concentrations. From solutions containing both these acids, anion sorption depends on both pH and anion fraction. Electrokinetic properties of zirconia in these solutions have been studied by microelectrophoresis. Zirconia is negatively charged in water, charge reversal occurring in nitric acid and hydrochloric acid solutions at concentrations $\sim 10^{-4}$N and $\sim 10^{-3}$N, respectively.

HYDRATED metal oxides form part of a group of inorganic materials which are of interest in the field of ion-exchange, behaviour comparable to that of the synthetic organic exchangers having been demonstrated in some circumstances.[1] The electrokinetic properties of a number of metal oxide surfaces in acid solutions have been discussed [2] in terms of anion-exchange with surface hydroxyl groups, accompanied by the process of physical adsorption. The relative importance of these processes depends upon the anions present and particularly on the pH of the solution. Anderson,[3] in an electrophoretic study of thoria dispersions, considered the dissociation of surface hydroxyl groups to be equivalent to the adsorption of hydrogen and hydroxyl ions on a giant zwitterion represented by $>Th^{+}-O^{-}$.

It has been shown [4,5] that interpretation of electrokinetic data in terms of adsorption processes may be misleading since such data give information regarding only the net charge on either side of the slipping plane. In the present work the processes occurring at the zirconia/solution interface have been examined by consideration of electrokinetic data in conjunction with direct measurements of the extent of sorption by the solid from solution.

EXPERIMENTAL

Materials.—High-purity zirconia, supplied by Johnson Matthey and Company Ltd., was crushed in an agate mortar and fractionated by differential sedimentation in distilled water. Two samples were employed for sorption measurements: I, particle size range 200—500 μ in diam.; II, 400—600 μ in diam. Fines, 1—2 μ in diam., were separated for microelectrophoretic studies. All samples were repeatedly washed with boiling conductivity water and dried at 110°. Conductivity water, of specific conductivity $2—4 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$, was prepared by an ion-exchange process. " AnalaR " nitric and hydrochloric acid were diluted to ~ 0.1N-concentration and standardised against borax. More dilute solutions were made up by weight from the 0·1N-solutions. " AnalaR " sodium chloride was recrystallised from conductivity water and solutions made up by weight.

Apparatus and Procedure.—Sorption measurement. Zirconia was equilibrated with conductivity water and additions of stock electrolyte solution were made from a weight burette.

[1] Kraus, Phillips, Carlson, and Johnson, Proc. 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. XXVIII, United Nations, Geneva, 1958; Amphlett, McDonald, and Redman, *J. Inorg. Nuclear Chem.*, 1958, **6**, 236.

[2] O'Connor and Buchanan, *Austral. J. Chem.*, 1953, **6**, 278; 1957, **10**, 398; O'Connor, Johansen, and Buchanan, *Trans. Faraday Soc.*, 1956, **52**, 229.

[3] Anderson, *Trans. Faraday Soc.*, 1958, **54**, 130.

[4] Benton, Elton, and Harrison, *J.*, 1960, 4019.

[5] Benton and Horsfall, *J.*, 1962, 3899.

After each addition the conductance of the solution was measured, and also, for solutions containing hydrochloric acid, the e.m.f., E, of the cell

$$\text{Glass electrode/Solution/Ag–AgCl electrode}$$

where
$$E = \frac{2 \cdot 303 \boldsymbol{R}T}{\boldsymbol{F}} \log \frac{1}{C_{\mathrm{H}} \cdot C_{\mathrm{Cl}}} + \text{Constant.}$$

The apparatus, procedure, and prior calibration of the measuring systems have been described previously.[5] Determinations were carried out at $25° \pm 0\cdot01°$.

Electrophoretic measurements. A stock suspension of zirconia fines (cf. above) was prepared from $1\cdot2$ g. of the material in 100 ml. of conductivity water. Suspensions for electrophoretic examination were prepared by adding $0\cdot4$ ml. of stock suspension to 100 ml. of the appropriate electrolyte solution. Suspensions were shaken mechanically for $\ll 1$ hr. before use.

The cell employed was essentially of the Mattson type [6] but was used with the capillary mounted vertically. The Pyrex capillary, 28 cm. long and $0\cdot125$ cm. radius, having two out-side faces at right angles ground optically flat, terminated at each end in an electrode chamber. Electrodes were of greyed platinum sheet, 4 cm. $\times$ 1 cm., and a potential gradient of $6\cdot25$ v/cm. was employed. Particles were viewed with a microscope set horizontally at right angles to the illumination from a 24-w lamp and condenser system. The objective was $\times 10$ and the eye-piece $\times 20$. Observations of particle velocities, in the calculated stationary level,[6] were made for each direction of the electric field, *i.e.*, with and against gravity. In focussing at the stationary level, allowance was made for the optical effect of the plano-concave lens of the cell wall as shown by Henry.[7] Velocities were measured, by timing the passage of particles across a calibrated eye-piece graticule, with two stop watches in order that continuous observation of a given particle could be maintained for each direction of the field. If v_1 and v_2 are particle velocities with upper and lower electrodes positive, respectively, V_{g} is the sedimentation velocity in absence of a field and V_{E} the electrophoretic velocity, then $v_1 = V_{\mathrm{g}} + V_{\mathrm{E}}$, $v_2 = V_{\mathrm{g}} - V_{\mathrm{E}}$, $V_{\mathrm{E}} = (v_1 - v_2)/2$.

Results

Sorption Measurements.—No sorption from pure sodium chloride solutions was detected, measured conductances of solutions in equilibrium with the zirconia being identical with those in absence of zirconia. The smallest sorption detectable with reasonable accuracy, in the systems employed here, was $\sim 10^{15}$ ions/g. at 10^{-5}N-equilibrium solution concentration and $\sim 10^{17}$ ions/g. at 10^{-3}N.

Sorption from hydrochloric acid solutions was measured by conductometric and potentio-metric techniques and excellent agreement of results from the two methods was obtained throughout the concentration range studied. Results are illustrated in Fig. 1. α is the number of chloride ions sorbed per g. of zirconia, calculated by using the equation, $\alpha = (C_0 - C_{\mathrm{E}})VN/10^3W$, where $C_0 =$ normality of solution in absence of sorption, $C_{\mathrm{E}} =$ normality of solution, volume V c.c., in equilibrium with W g. of zirconia. Results obtained for zirconia samples I and II were in a constant ratio over the whole concentration range studied. This is doubtless a reflection of proportionality between particle size and number of available sorbing sites.

The sorption isotherm, determined conductometrically, for zirconia sample II in nitric acid solutions is also illustrated in Fig. 1.

Equilibrium in the acid solutions was attained in about 2 hr. although $\sim 90\%$ the sorption occurred within a few minutes. Replacement of the equilibrium solution with conductivity water showed very slight reversibility of the sorption. Sorbed anions could be removed by repeated washing with boiling conductivity water and only after such treatment could sorption isotherms be accurately reproduced.

Sorption by zirconia, sample I, from solutions containing equimolar quantities of sodium chloride and hydrochloric acid was studied in the concentration range 2×10^{-5}N to 2×10^{-3}N

[6] Mattson, *J. Phys. Chem.*, 1933, **37**, 223.
[7] Henry, *J.*, 1938, 997.

with respect to chloride ion. Equilibrium ionic concentrations were calculated from the equations

$$C_H + C_{Na} = C_{Cl};$$

$$10^3 K = C_H \cdot \Lambda_{HCl} + C_{Na} \cdot \Lambda_{NaCl};$$

$$f(E) = C_H \cdot C_{Cl}.$$

Equivalent-conductance values, Λ, were taken, initially, as those valid at the total ionic strength of the solution on the assumption that no sorption had occurred. Successive approximation was carried out to obtain values valid at the total ionic strength of the equilibrium solution.
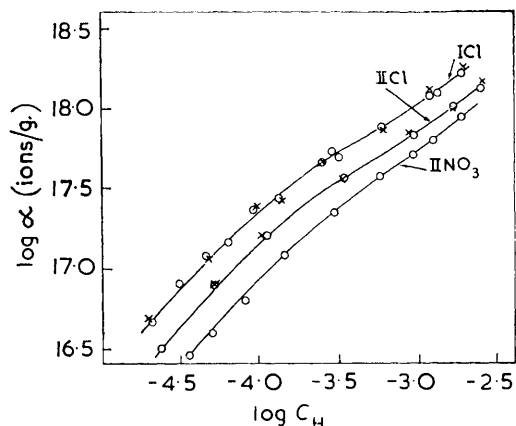
FIG. 1. Sorption from hydrochloric and nitric acid solutions. Curve ICl, ZrO_2 sample I–HCl; Curve IICl, ZrO_2 sample II–HCl; Curve IINO$_3$, ZrO_2 sample II–HNO$_3$. × Potentiometric; ○ conductometric.
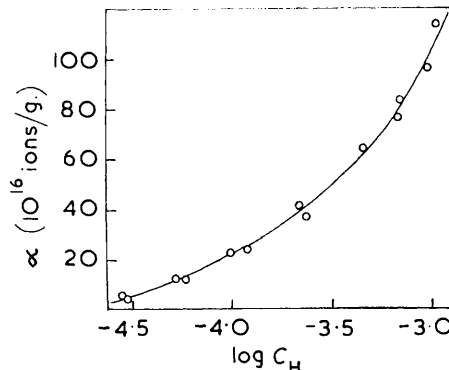
FIG. 2. Sorption of chloride ion by ZrO_2, sample I, from solutions equimolar with respect to sodium chloride and hydrochloric acid. Full curve: sorption from pure hydrochloric acid solutions.

Calculated values of C_{Na} showed that no sorption of sodium ion occurred and the sorption of chloride ion was solely pH-dependent. This is illustrated in Fig. 2 where α_{Cl} is shown plotted as a function of equilibrium hydrogen-ion concentration. The full curve is the sorption isotherm for pure hydrochloric acid solutions.

Sorption of chloride and nitrate ions from solutions containing hydrochloric and nitric acid was studied in the concentration range 2×10^{-5}N to 2×10^{-3}N with respect to hydrogen ion. Determinations were made for three different concentration ratios of the acids in solution, namely, $3 : 1$, $1 : 1$, and $1 : 3$.

Equilibrium ionic concentrations were calculated from the equations

$$C_H = C_{NO_3} + C_{Cl};$$

$$10^3 K = C_{NO_3} \Lambda_{HNO_3} + C_{Cl} \Lambda_{HCl};$$

$$f(E) = C_H \cdot C_{Cl}.$$

Results are illustrated in Figs. 3a—c where values of α_{Cl} and α_{NO_3}, the numbers of chloride and nitrate ions sorbed, are plotted as a function of equilibrium hydrogen-ion concentration. Since sorption of the two anions was not equivalent, the anion concentration ratio in solution changed during a run. The limits of such change are indicated for the appropriate figures.

The relative extent of sorption of chloride and nitrate ions is seen to be a function of pH and of anion fraction in solution. The general tendency for relatively greater sorption of the anion present in greater concentration in solution is superimposed on an increased preference for sorption of chloride ion as the pH of the solution is lowered.

8 A

Electrophoretic Measurements.—Electrophoretic mobilities of zirconia have been measured in conductivity water and solutions of hydrochloric acid, nitric acid, and sodium chloride in the concentration range 10^{-5}N to 10^{-2}N.
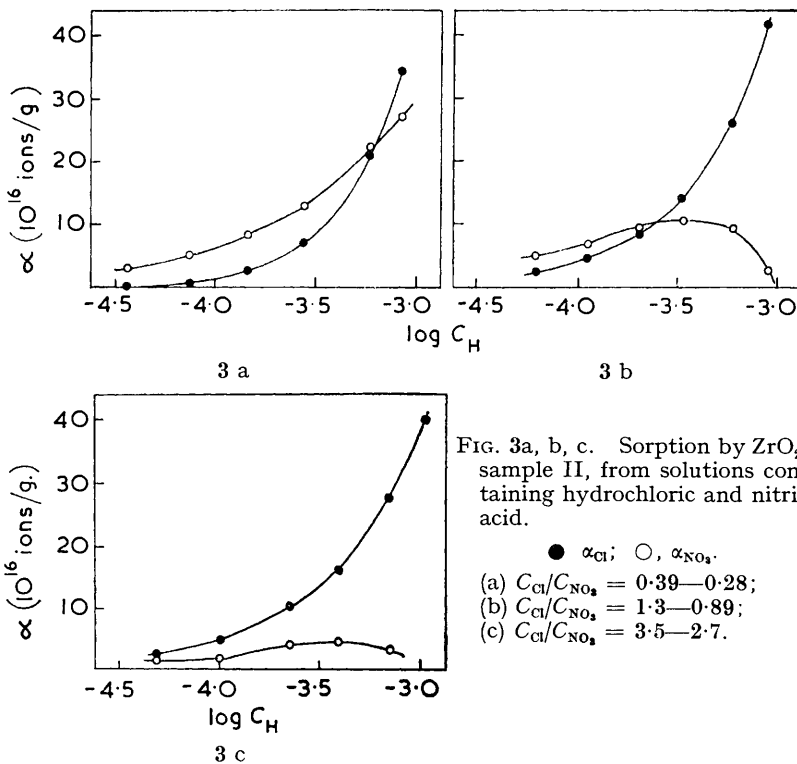

3 a

3 b

3 c

Fig. 3a, b, c.   Sorption by ZrO_2, sample II, from solutions containing hydrochloric and nitric acid.

● α_{Cl}; ○, α_{NO_3}.

(a) C_{Cl}/C_{NO_3} = 0·39—0·28;
(b) C_{Cl}/C_{NO_3} = 1·3—0·89;
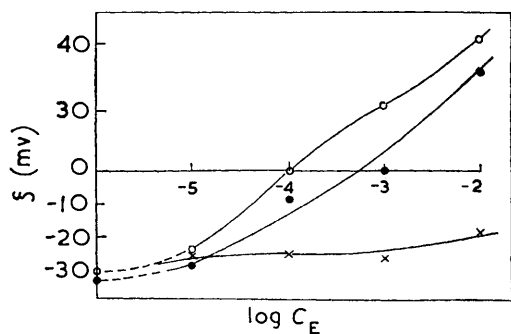(c) C_{Cl}/C_{NO_3} = 3·5—2·7.

Fig. 4.   Electrokinetic potentials of zirconia in hydrochloric acid (●), nitric acid (○), and sodium chloride solutions (×).
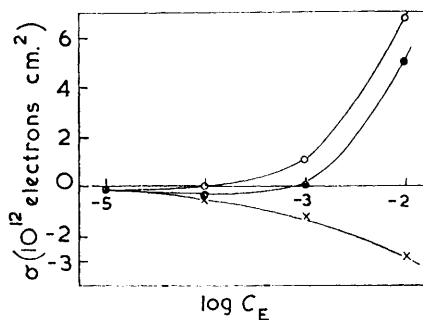

Fig. 5.   Electrokinetic charges of zirconia in hydrochloric acid (●), nitric acid (○), and sodium chloride solutions (×).

Electrokinetic potentials were calculated from the classical equation $\xi = 4\pi\eta V_E/\varepsilon E$, where V_E is the particle velocity under an applied field strength E in a dispersion medium of dielectric constant ε and viscosity η.   The numerical factor 4 was adopted throughout since corrections for relaxation and surface conductance effects,[8,9] would be small for the particle sizes (diam.

[8] Booth, *Nature*, 1948, **161**, 83.
[9] Booth, *Trans. Faraday Soc.*, 1948, **44**, 955.

1—2 μ) and low electrokinetic potentials encountered in the present work in uni-univalent electrolytes.

In conductivity water the electrokinetic potential obtained ranged from $-29\cdot4$ to $-32\cdot8$ mv. Results in the electrolyte solutions are illustrated in Fig. 4. Corresponding values of the electrokinetic charge, σ, *i.e.*, the net charge density on the solid side of the electrokinetic plane of slip have been calculated from the equation [10]

$$\sigma = \left(\frac{2n\,\varepsilon\,\boldsymbol{k}T}{\pi}\right)^{\frac{1}{2}}\sinh\frac{e\,\xi}{2\boldsymbol{k}T}$$

where n = electrolyte concentration in ions/c.c. Results are illustrated in Fig. 5.

DISCUSSION

The processes occurring may be considered to involve the dissociation, and exchange with ions from solution, of amphoteric hydroxyl groups on the surface regions of the zirconia, together with physical adsorption of ions from solution. The negative surface charge in water indicates a predominant acidic dissociation across the electrokinetic slipping plane, while in acid solutions promotion of basic dissociation provides positive sites for anion sorption by exchange. The number of sites available for anion sorption thus depends, in the first place, on hydrogen-ion concentration, but superimposed upon this effect will be the effect of the particular anion sorbed. The electrokinetic data (Fig. 5) show the isoelectric point of zirconia to occur at a lower concentration in nitric acid than in hydrochloric acid. Mattson and Pugh [11] suggested that ions such as chloride and nitrate are more covalently bound than the hydroxyl ion and that the isoelectric pH is determined by the degree of dissociation of the surface complex formed with the anion. Thus, in accord with the complex chemistry of these ions, the isoelectric points suggest that the nitrate ion is held by a bond less covalent in character than that holding the chloride ion. The greater positive charge, at a given pH, in nitric acid than in hydro-chloric acid solution would tend to lower the basic dissociation, thereby reducing the number of available sites for further anion sorption. The total-sorption measurements (Fig. 1) confirm that chloride ion is sorbed to greater extent than nitrate ion throughout the pH range studied.

An interdependence of sorption sites is again reflected by the results in mixed solutions of sodium chloride and hydrochloric acid, where chloride-ion sorption is governed by pH and not by chloride-ion concentration. Anderson,[3] in an electrokinetic study of thoria dispersions, described the dissociation processes in terms of a Langmuirian model, thus implying independence of sorption sites. However, he found departures from the model in hydrochloric acid solutions.

Comparison of the magnitude of total sorption from the acid solutions (Fig. 1) with that of corresponding electrokinetic charges (Fig. 5) demonstrates that a large proportion of the sorption is not directly involved in determination of the properties of the interface governing electrokinetic behaviour. As found in other systems [4,5] the present results indicate considerable sorption in regions of the particle structure on the solid side of a relatively non-re-entrant slipping surface around the particle.

In solutions containing both nitric and hydrochloric acid, the basic dissociation is modified by both anions. From Fig. 3a it is seen that, when the nitrate : chloride con-centration ratio in solution was high, sorption of nitrate ion was predominant at pH values greater than ∼3·2. Thus a probability factor dependent on anion fraction is exhibited, the preference for chloride sorption off-setting this factor when exchange was greater at the lower pH values.

At low hydrogen-ion concentrations the physical adsorption of ions may be important.

[10] Verwey and Overbeek, " Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.
[11] Mattson and Pugh, *Soil. Sci.*, 1934, **38**, 299.

This would explain the greater sorption of nitrate ions from solutions of lower hydrogen-ion concentration containing equal proportions of the anions (Fig. 3b). Again, at higher hydrogen-ion concentrations, chloride-ion sorption predominated and in fact exchange of sorbed nitrate ions for chloride ions is indicated.