768. *Sorption from Some Electrolyte Solutions by Synthetic Magnetite.*

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Measurements have been made of the extent of sorption by magnetite from a number of electrolyte solutions, by determination of concentration loss from solution, in the range 2×10^{-5}—2×10^{-3}N. It is suggested that sorption from almost neutral salt solutions arises by exchange with amphoteric groups in a hydrated magnetite lattice. In hydrochloric acid, ferrous ions are released into solution. The results are compared with results of electrokinetic studies of adsorption in similar systems.

Phenomena occurring at the interface between a metallic oxide and an aqueous electrolyte solution have aroused considerable interest and have been the subject of many electrokinetic studies. These phenomena are doubtless of importance in the aqueous corrosion of metals, where the presence of an oxide film on the metal raises the question of a possible connection between adsorption at the oxide–solution interface and corrosion processes or the mode of action of corrosion inhibitors.

Magnetite is frequently found as a corrosion product of steels. Anderson [1] has attempted a comparison between the inhibitory action of a number of anions and their adsorbability on this oxide. The adsorption was investigated by examining the electrophoretic behaviour of magnetite dispersions in chloride solutions of different pH and in various pure unbuffered electrolyte solutions. The measurement of electrophoretic mobilities of particles in a suspension enables electrokinetic (ζ) potentials to be determined directly.

However, as pointed out by Anderson, the calculation of adsorption data from such determinations requires a number of assumptions regarding the structure of the interfacial electric double layer, in particular concerning the location of the electrokinetic slipping-plane. The " adsorption " data derived from electrokinetic measurements are therefore usually limited to the net charge of the adsorbed " layer " on either side of the slipping-plane. It follows that, unless evidence is available to show that only ions of one sign are adsorbed into the region on the surface side of the slipping-plane, considerable caution is required in drawing conclusions from electrokinetic measurements regarding the extent of adsorption of a given species.

The work described here represents part of a wider study, of adsorption by powdered solids from electrolyte solutions, in which direct determinations of concentration loss from solution have been made by using conductometric and potentiometric techniques.

Experimental

Materials.—Magnetite was prepared by three methods.

Preparation I was obtained as described by Welo and Baudisch.[2] A solution of ferrous sulphate was added slowly with stirring to a solution of sodium hydroxide containing potassium nitrate. When this mixture was set aside the green precipitate gave magnetite. This was repeatedly washed with conductivity water and consisted of particles in the size range 1—2 μ diameter.

Preparation II was obtained as described by Anderson.[1] A solution of ferrous sulphate and ferric chloride was treated with an excess of concentrated ammonia solution, and the product was repeatedly washed with conductivity water. The preparation gave particles in the size-range 3—10 μ but contained much agglomerated material which peptised in acid solution. For work in the hydrochloric acid solutions, therefore, the well-washed product

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[1] Anderson, Proc. 2nd International Congress on Surface Activity, Vol. III, Butterworths, London, 1957, p. 67.

[2] Welo and Baudisch, *Phil. Mag.*, 1927, **3**, 396.

was separated and heated in a Pyrex boat at 300—400° for 30 min. in a rapid stream of nitrogen. The hard product was ground and particles in the size-range 5—20 μ diameter separated from finer material by differential sedimentation in conductivity water.

Preparation III was obtained by the dry method described by David and Welch.[3] Mond carbonyl Iron Powder (grade MCP) and highly pure ferric oxide (Johnson Matthey) were intimately mixed in stoicheiometric proportion and heated in a current of purified argon at 960° for 6 hr. The magnetite obtained was in the particle-size range 5—20 μ diameter.

Conductivity Water.—This was prepared by an ion-exchange process; its specific conductivity was 2—4 $\times 10^{-7}$ ohm^{-1} cm.$^{-1}$. " AnalaR " hydrochloric acid was diluted to $\sim$0·1N; it was standardised volumetrically with borax. More dilute stock solutions were made up by weight from the 0·1N-solution. " AnalaR " salts were recrystallised, where applicable, from conductivity water.

Apparatus and Procedure.—The method adopted for the determination of concentration-loss from solution, in the concentration range 2×10^{-5}N—2×10^{-3}N, consisted of equilibration of adsorbent with conductivity water followed by addition of stock electrolyte solution in small quantities from a weight burette. After each addition, the electrical conductance of the solution was measured, and also, in the case of hydrochloric acid solutions, the e.m.f., E, of the cell

Glass electrode/Solution/Ag–AgCl electrode,

where

$$E = (2{\cdot}303\boldsymbol{R}T/\boldsymbol{F}) \log 1/(C_{\mathrm{H}}.C_{\mathrm{Cl}}) + \text{Constant},$$

i.e., $C_{\mathrm{H}}.C_{\mathrm{Cl}} = \mathrm{f}(E)$.

Prior calibration of the measuring systems was carried out by blank runs, in the absence of adsorbent; hence equilibrium concentrations in an adsorption run could be obtained. The apparatus was a modification of that described by Benton, Elton, and Harrison,[4] for conductometric determination of concentration loss, an extra side-chamber having been added to accommodate the reversible-electrode system. Equilibration of the solid and the solution, after each addition of electrolyte, was carried out, with stirring, in a main compartment, after which supernatant solution could be forced by nitrogen into subsidiary chambers for conductometric and potentiometric measurements. The apparatus was kept in an oil-bath at 25° ± 0·01°. The conductance measurements, with bright platinum electrodes, were made by using a conventional a.c. bridge, with the oscillator operating at 1000 c./sec. The reversible-electrode system consisted of a glass electrode (manufactured by Electronic Instruments Limited for use with the " Vibron " electrometer) and a silver–silver chloride electrode mounted in a rubber bung. This system was placed in the experimental solution only when a reading was taken; at other times it was immersed in another container, also in the thermostat, containing 10^{-4}N-hydrochloric acid. Measurements of the e.m.f. of the resulting cell at frequent intervals during an adsorption run enabled any variation in the asymmetry potential of the electrode system to be followed, and errors therefrom in the concentration-loss measurements to be eliminated. The e.m.f. determinations were made with a Tinsley potentiometer, type 3387 B, with a " Vibron " electrometer (Electronic Instruments Ltd.) as a null detector. The electrometer and potentiometer stood on copper sheets connected to a common earth. The metal framework supporting the experimental cell was also connected to the common earth as was the shielding of the leads to the cell. These precautions were essential to obtain steady and reproducible measurement of potential. With this apparatus measurements from 0 to 450 mv could be made, and in the systems studied here reproducibility of the potential readings was within 0·05 mv.

Measurements were also made of concentration-loss from solutions of sodium chloride of concentration greater than in the above experiments. After equilibration of a known weight of magnetite with a solution of known concentration, a quantity of the solution was removed and analysed by conductometric titration with silver nitrate solution. The addition of ethyl alcohol to the titration cell[5] allowed determination of the end-point with the necessary precision within the range of equilibrium concentration 5×10^{-4}N—5×10^{-1}N.

[3] David and Welch, *Trans. Faraday Soc.*, 1956, **52**, 1642.

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

[5] Strouts, Gilfillan, and Wilson, " Analytical Chemistry," Vol. II, Oxford University Press. 1955.

RESULTS

Sorption from sodium chloride solutions by magnetite, Preparation I, is illustrated in Fig. 1. Here, α represents the numbers of sodium or chloride ions sorbed per g. of magnetite, calculated by using the equation, $\alpha = (C_0 - C_E)VN/1000W$, where C_0 = normality of solution in absence of magnetite, C_E = normality of solution in equilibrium with W g. of magnetite, and V = volume of solution. Results indicated for concentrations greater than approx. 10^{-3}N, in this Figure, were obtained by conductometric titration. A Freundlich isotherm $\alpha = k_1 C_E^{k_2}$, where k_1 and k_2 are constants, is satisfied by this sorption for equilibrium concentrations greater than approx. 2×10^{-4}N.

All other work on sorption from salt solutions was carried out with magnetite, Preparation II, since direct comparison of the results with electrophoretic data [1] available for this preparation could then be made. Results for sorption from sodium chloride, sodium sulphate, potassium chromate, and disodium hydrogen phosphate solutions are illustrated in Fig. 2. Here, α represents ions sorbed in equivalents per g. of magnetite. Sorption from sodium benzoate solutions was found to be less than is detectable by the present technique, the conductances of solutions in equilibrium with magnetite being identical with those in the absence of magnetite.

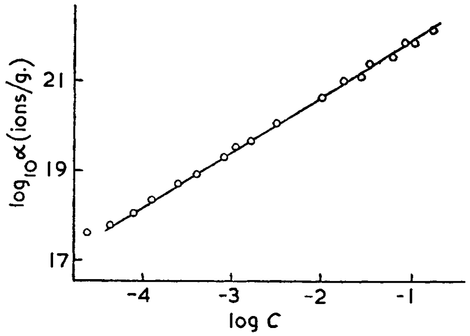

FIG. 1. Sorption of sodium chloride by magnetite, Preparation I.

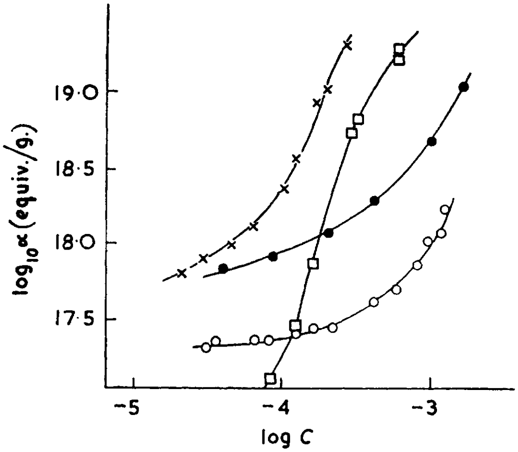

FIG. 2. Sorption by magnetite, Preparation II. ○ NaCl; ● Na_2SO_4; □ Na_2HPO_4; × K_2CrO_4.

The sorption from sodium chloride and sodium sulphate solutions was irreversible, in that no desorption was detected on exchange of the solution, at the end of a sorption run, for fresh conductivity water.

The sorption from disodium hydrogen phosphate and potassium chromate solutions was accompanied by some peptisation of the magnetite at concentrations greater than approx. 10^{-4}N. The rapid increase in the extent of sorption from these solutions is likely to be at least partly due to an increase in available sorbing sites on the magnetite arising from this phenomenon. However, the sorption from these solutions was reversible.

In hydrochloric acid solutions, simple sorption of hydrogen chloride would be determinable from two independent measurements of concentration loss, namely the potentiometric and conductometric measurements. However, simple sorption was not obtained since calculated equilibrium concentrations of hydrogen chloride from conductometric and potentiometric measurements differed considerably. The divergence suggested the presence of a third ion in the equilibrium solutions. This has been shown to be the ferrous ion. No trace of ferric ion has been detected by using ammonium thiocyanate as a spot test. The experimental conductometric and potentiometric data have therefore been interpreted in terms of the three species H^+, Cl^-, and Fe^{2+}, and the equilibrium concentrations (c g. equiv./l.) by using the equations

$$10^3\kappa = c_H\lambda_H + c_{Cl}\lambda_{Cl} + c_{Fe}\lambda_{Fe},$$

$$(E) = c_H \cdot c_{Cl}, \text{ and } c_H + c_{Fe} = c_{Cl},$$

where κ = specific conductivity of the solution, and λ = ion conductance at the appropriate ionic strength. A typical series of results is given in Table 1.

TABLE 1.

Adsorption by magnetite (5·49 g.) from hydrochloric acid solution.

[Concns. are g.-equiv./l.]

Vol. of solution (c.c.)	10^4C_0	C_{H^+}	$10^4C_{Cl^-}$	$10^4C_{Fe^{2+}}$
116·06	1·09	$1·45 \times 10^{-7}$	1·05	1·05
118·23	2·35	$7·69 \times 10^{-7}$	2·22	2·11
121·82	4·34	$2·43 \times 10^{-6}$	3·67	3·64
128·36	7·69	$9·76 \times 10^{-6}$	5·61	5·52
138·08	12·1	$3·60 \times 10^{-5}$	8·00	7·64
140·21	37·3	$1·14 \times 10^{-4}$	26·1	25·0
143·32	73·0	$1·65 \times 10^{-4}$	54·8	53·2

C_0 = concn. of hydrochloric acid if no sorption or other action took place. C = equilibrium concn.

TABLE 2.

Adsorption by magnetite (2·56 g.) from $4·695 \times 10^{-4}$N-hydrochloric acid solution.

Solution in equilibrium successively exchanged. Concns. are g.-equiv./l.

Stage	Total vol. solution used (c.c.)	$10^5C_{H^+}$	$10^4C_{Cl^-}$	$10^4C_{Fe^{2+}}$	$10^4C_{Fe^{2+}}$ (colorimetric)
1st equilibn.	120	1·45	4·45	4·30	5·20
5th ,, ...	600	1·94	4·53	4·34	4·46
10th ,, ...	1100	2·49	4·61	4·36	4·44
15th ,, ...	1600	7·37	4·60	3·86	3·42
20th ,, ...	2100	8·55	4·63	3·78	3·32

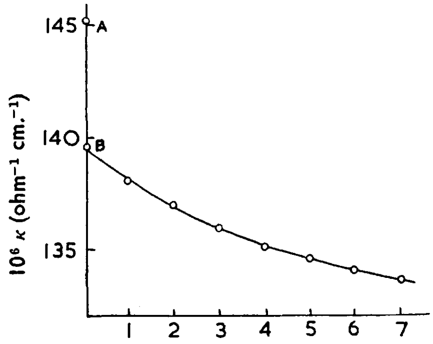

FIG. 3. Addition of 4·2 g. of magnetite, (Preparation III) to 125 of g. $3·42 \times 10^{-4}$N-hydrochloric acid. Variation of specific conductance of solution with time. A, specific conductance in absence of magnetite; B, specific conductance immediately after addition of magnetite.

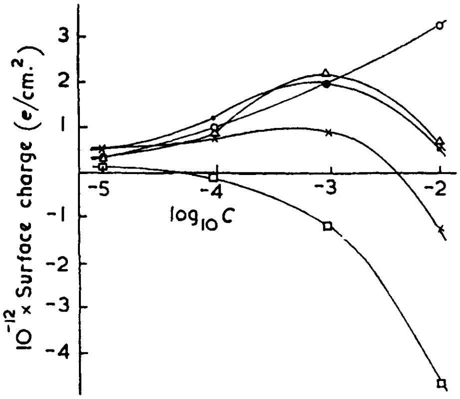

FIG. 4. Electrophoretic data for magnetite, Preparation III (Anderson [1]). ○ NaCl; ● Na_2SO_4; □ Na_2HPO_4; × K_2CrO_4; Δ sodium benzoate.

Further studies in hydrochloric acid have been made by repeated exchange of the solution in equilibrium with magnetite, Preparation II, for a solution of hydrochloric acid of one particular concentration. After equilibration of magnetite and solution, the concentrations of the three ionic species were determined. The supernatant solution was then removed, and was replaced by a similar weight of the hydrochloric acid solution, and equilibrium concentrations were again determined. Results obtained by this repeated procedure are illustrated in Table 2 for the case of approx. 5×10^{-4}N-hydrochloric acid. In the early stages, equilibrium was attained in less than 1 hr., this time lengthening to 20 hr. in the later stages.

Ferrous ions were also found to be released in hydrochloric acid solutions by magnetite, Preparation III, but much more slowly than in the case of the precipitated magnetites. The results indicate a very rapid sorption from solution, followed by a further slow process or processes as ferrous ions enter solution. The effect is illustrated in Fig. 3, where the change in conductance of the solution with time is given for the case of the first equilibration of magnetite, Preparation III, with $3{\cdot}42 \times 10^{-4}$N-hydrochloric acid.

DISCUSSION

It is of interest to compare the present results for sorption from pure unbuffered salt solutions with the corresponding electrophoretic data obtained by Anderson.[1] To facilitate such a comparison the "surface" charge data given by this author are reproduced in Fig. 4. It is apparent that a quite different picture of the relative adsorbability of the various ions studied is given. The most striking contrast is between the similarity of the electrophoretic data for the benzoate, chloride, and sulphate solutions and lack of corresponding similarity in the present data, where, in particular, sorption from benzoate solutions was not detectable.

It has been demonstrated [6] that hydrous oxides show exchange between amphoteric hydroxyl groups on the lattice and ions in solution, and it is suggested that such a mechanism occurs in the present case. This view is supported by the finding that the extent of sorption of sodium chloride by magnetite prepared in the dry way (Preparation III) was less than that by the precipitated magnetites by 1—3 orders of magnitude. This would seem most likely as the result of a relatively open hydrated particle structure in the precipitated magnetite, allowing more (exchange) sorption within the re-entrant regions of the particles. It is also apparent that at the pH of the salt solutions, cation- and anion-exchange both occur. The separate occurrence of either would be accompanied by pH changes in the bulk solution, which were not observed, and also by a rise of conductance in the bulk solution rather than the observed fall in conductance by which the sorption was measured.

Anderson concluded, apparently on the basis of the continuous increase of surface-charge with increasing concentration of sodium chloride solution, that chloride ion is not adsorbed by magnetite. The present work demonstrates that such a conclusion is ill-advised. It is suggested that electrophoretic "adsorption" data merely reflect the charge (which indeed is likely to be a *net* charge) arising from ions at either side of a relatively non-re-entrant slipping surface around a particle. Yet a large number of ions may be sorbed in the re-entrant regions of the particles and these play little part in determining the properties of the interface governing electrophoretic particle mobility. The fact that sorption from sodium benzoate solutions was not detected by the present technique may arise from the inability of the large benzoate ion to penetrate the re-entrant regions of the magnetite.

In hydrochloric acid solutions it is seen from Tables 1 and 2 that the removal of hydrogen ion from solution is very great. That the interpretation of the experimental conductivity and e.m.f. data is essentially correct has been confirmed by colorimetric determination of ferrous ion in the equilibrium solutions, with *o*-phenanthroline, by using a Unicam S.P. 500 spectrophotometer at a wavelength of 500 mμ. The procedure described by Vogel [7] was employed. Results of these determinations are illustrated in Table 2.

Anderson [1] concluded that the effect of pH on the net surface charge of magnetite in aqueous chloride solution, determined by electrophoresis, was attributable to the influence on the extent of dissociation of basic groups on the hydrated surface. This interpretation was, in fact, found to be least satisfactory at low pH. In electrophoretic studies a small quantity of solid is equilibrated with a relatively great volume of electrolyte solution, with the result that the phenomena made apparent by the present work (in which the ratio of

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[6] Amphlett, McDonald, and Redman, *J. Inorg. Nuclear Chem.*, 1958, **6**, 336.

[7] Vogel, "Textbook of Qualitative Inorganic Analysis," IVth edn., Longmans, London, 1955.

the weight of solid to the volume of solution is relatively enormous) would lead to negligible changes in the composition of the solution. However, from the point of view of the structure of the solid and the nature of its surface, these phenomena should be considered in any interpretation of electrophoretic data.

In conclusion, the present work demonstrates that data regarding extent of adsorption or relative adsorbability of different ions, derived from electrokinetic studies, must be considered with caution, unless taken in conjunction with studies of total sorption, particularly in any application such as a comparison with the corrosion inhibiting properties of ions.

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