793. *Adsorption from Hydrochloric Acid, Sulphuric Acid, and Potassium Chloride Solutions by Gold.*

By D. P. Benton, G. A. H. Elton, and J. T. Harrison.

Measurements of the extent of ion adsorption by gold powder from dilute solutions of hydrochloric acid, sulphuric acid, and potassium chloride have been made conductometrically. Adsorption from hydrochloric acid is several times greater in extent and considerably less reversible than that from potassium chloride or sulphuric acid solutions. Consideration of the results in the light of appropriate electrophoretic data shows that the extent of cation adsorption into the diffuse part of the electrical double layer is only a small fraction of that into the region on the solid surface side of the electrokinetic slipping plane. Adsorption processes at such interfaces cannot, therefore, by interpreted by consideration only of electrokinetic data.

It is known that the presence of adsorbed films of ions on the surface of metal powders can have marked effects on the metallurgical properties of the powders. For example, it has been found that some sintering and hot-compacting processes are improved by washing the metal powder with certain aqueous solutions.[1] The present paper describes part of an investigation of the extent and nature of adsorption by metal powders from electrolyte solutions.

The adsorption of ions by mercury has been extensively studied,[2] largely because the extent of adsorption is determinable from measurements of interfacial tension, *e.g.*, by using a capillary electrometer. For the large majority of ions investigated, physical adsorption predominates, although certain ions, *e.g.*, sulphide, can be chemisorbed. Adsorption by other metals has been studied less extensively. Some measurements have been made on platinum,[3] and on silver and copper.[4–6] Techniques employed have involved, *inter al.*, the measurement of electrode capacities,[7] contact angles of gas bubbles on the surface,[8] electrophoretic mobilities,[3] and adsorption of radioactive tracers.[6,9,10]

In the work described here, in order to minimise complications due, for example, to corrosion or formation of oxide films, studies have been made of the adsorption of ions by gold powder. The extent of adsorption has been determined by measuring the change in conductivity when an electrolyte solution is equilibrated with a large surface area of gold powder.

Experimental

Materials.—Precipitated gold powder was supplied by Johnson Matthey and Company Ltd. and specimens in the particle size range 10—40 μ were separated by fractional sedimentation in water. Specimens were washed in ether and acetone, repeatedly washed in conductivity water, and finally dried in a vacuum desiccator. Conductivity water was prepared by an ion-exchange process; its specific conductivity was 2—4 × 10^{-7} ohm^{-1} cm.^{-1}. "AnalaR" hydrochloric and sulphuric acids were diluted to approx. 0·1N-concentration and standardised volumetrically by borax. More dilute stock solutions were made up by weight from the 0·1N-solutions. "AnalaR" potassium chloride was recrystallised several times from conductivity water, heated to dull redness in a platinum dish, and allowed to cool in a vacuum desiccator.

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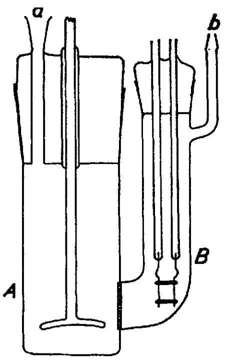
[1] See, *e.g.*, Goetzel, "Treatise on Powder Metallurgy," Interscience, New York, 1949, Vol. I, p. 263.
[2] Parsons, "Modern Aspects of Electrochemistry," Butterworths, London, Vol. 1, pp. 127—173.
[3] Bach and Balaschowa, *Nature*, 1936, **137**, 617.
[4] King and Schochet, *J. Phys. Chem.*, 1953, **57**, 895.
[5] King and Scharfstein, *J. Phys. Chem.*, 1954, **58**, 180.
[6] King and Levy, *J. Phys. Chem.*, 1955, **59**, 910.
[7] Hanson and Clampitt, *J. Phys. Chem.*, 1954, **58**, 908.
[8] Moller, *Ann. Physik*, 1908, **27**, 665.
[9] Hackerman and Stephans, *J. Phys. Chem.*, 1954, **58**, 904.
[10] Erbacher, Herr, and Wiedmann, *Z. Naturforsch*, 1948, **3**, *A*, 637.

The specific surface areas of the gold powder specimens were determined by a modification of the catalytic decomposition of hydrogen peroxide method.[11] The method was standardised for gold by determination of the specific surface area of a specimen by using the B.E.T. krypton gas-adsorption technique. The gold powder used in these experiments had specific surface areas of 1—2 × 10^3 cm.^{2}.

Apparatus.—The apparatus was a modification of that described by Benton and Elton [12] and is shown in Fig. 1. Equilibration of powder and solution was carried out in the main cell *A*, of about 300 cm.^{3} capacity. The ground-glass stopper of this cell contained two inlet tubes, one of which was sleeved with a machined Nylon gland, through which passed a Pyrex glass stirrer; the other was used for addition of stock electrolyte solution and metal powder. The side arm *B* contained the electrode system and was separated from the main cell by a sintered (No. 3) glass disc. The apparatus was kept in an oil-bath at 25° ± 0·01°.

FIG. 1.



Procedure.—About 60 g. of gold powder were equilibrated with approx. 150 g. of conductivity water by rapid stirring. Clear solution could be forced into the electrode chamber by a stream of nitrogen entering at *a*. The conductivity was measured by use of a conventional a.c. bridge. Stock solution of electrolyte was then added in small quantities from a weight burette, equilibrium attained with rapid stirring, and the conductivity determined after each addition. For each electrolyte a blank run was carried out in which the resistances of the cell containing a number of solutions, accurately made up by weight, within the concentration range 10^{-5}—2×10^{-3}N, were determined. By using these data the equilibrium concentrations in an adsorption run could be obtained directly from conductance measurements. Desorption was studied by successive dilution of the solution; after the adsorbent powder had settled, weighed quantities of solution could be removed and replaced by conductivity water.

Results.—It was observed during preliminary experiments that the addition of the gold powder to conductivity water increased its conductivity, suggesting that dissolution or desorption of ionic material from the gold surface was taking place. Continued exchange of the water with fresh conductivity water did not enable the conductivity of the water in equilibrium with the gold to be reduced below approx. 3×10^{-6} ohm^{-1} cm.$^{-1}$. The time taken for an equilibrium conductivity reading to be obtained was about 36 hr. Conductivity determinations in solutions made up in water previously equilibrated with gold powder, showed that the conductivity of this water was additive to that of dissolved hydrochloric acid or potassium chloride. Hence, in the determinations of adsorption from solution discussed in this paper, the increase in conductivity on adding the gold powder was treated as a " solvent " correction and the quantity $\kappa_0 - (\kappa_m - \kappa_s)$ was regarded as a measure of the amount of added electrolyte adsorbed by the gold, where κ_0 = conductivity of added electrolyte if no adsorption took place, κ_m = measured conductivity, and κ_s = conductivity of water after addition of gold powder.

Values of α, the number of ions of each sign adsorbed at each sq. cm. of interface, were calculated from the equation

$$\alpha = N(c_0 - c_E)/1000\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c_0 = concentration of solution if no adsorption took place, c_E = equilibrium concentration after adsorption, determined conductimetrically, and θ = area of gold/volume of solution.

Adsorption from potassium chloride solutions was rapid, equilibrium being attained within the time taken to measure the conductivity of the solution. Moreover, it appeared that this adsorption was due to weak physical forces, since reproducible adsorption isotherms were obtained with a given specimen of gold powder after it had been washed several times within conductivity water. Adsorption from sulphuric acid solutions was similar in extent and nature to that from potassium chloride solutions. Fig. 2 shows results obtained for numbers of ions adsorbed, per cm.^{2} of interface, from solutions of potassium chloride and sulphuric acid, as a function of equilibrium concentration of the electrolyte. The points plotted were taken

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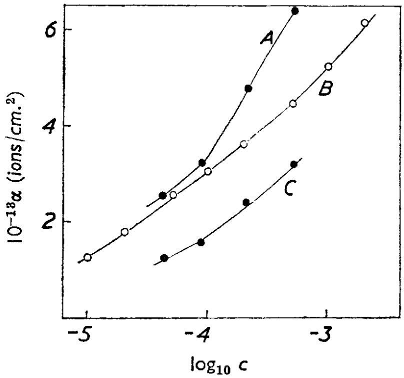
[11] Clark, *Paper Trade J.*, 1942, **32**, 115.

[12] Benton and Elton, *Trans. Faraday Soc.*, 1953, **49**, 1213.

from a smooth curve drawn through experimental points from several separate runs. These results were reproducible to within 5%.

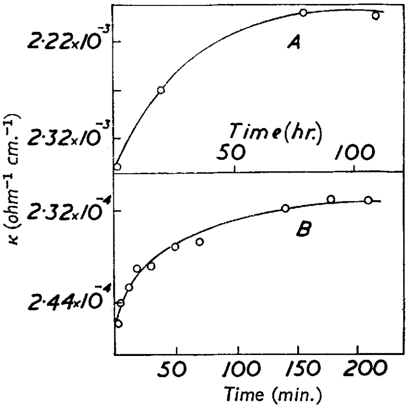
From hydrochloric acid solution adsorption was much slower, approx. 50% of the adsorption taking place within 30 min., and equilibrium being attained only after periods ranging from 3 hr. in the more dilute solutions to about 70 hr. in the more concentrated solutions. This effect is illustrated in Fig. 3 where the conductivity of the solution in contact with the powder is plotted against time. Fig. 4 shows the results obtained for the numbers of ions adsorbed at equilibrium, per cm.^{2} of interface, as a function of equilibrium concentration of hydrochloric acid. The broken line in this figure represents the desorption of hydrochloric acid from the surface and was obtained by progressive dilution of the solution with conductivity water. This indicates a considerable degree of irreversibility of the adsorption from hydrochloric acid solution. Gold powder used in adsorption determinations in hydrochloric acid had to be repeatedly washed in many changes of conductivity water over a period of a week before the adsorption isotherm could be reproduced.

FIG. 2.



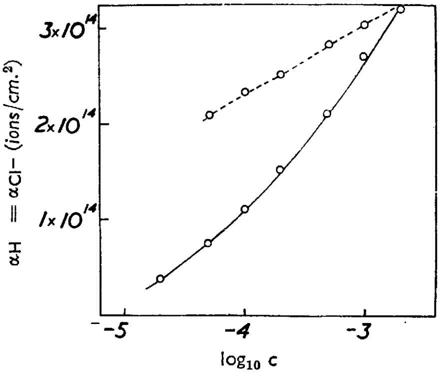
A, H^+. *B*, K^+, Cl^-. *C*, SO_4^{2-}.

FIG. 3.



A, $C_E = 1{\cdot}1 \times 10^{-3}$N.
B, $C_E = 1{\cdot}13 \times 10^{-4}$N.

FIG. 4.



DISCUSSION

It is suggested that the partly irreversible adsorption by gold from hydrochloric acid solution involves the formation, by chemisorption, of a surface gold chloride with further adsorption resulting in the formation of a surface chloroauric acid. The nature of the results for the adsorption from potassium chloride solution, however, indicates that in this case chemisorption is not involved. A possible explanation of this may be that the active adsorption sites for chemical Au–Cl interaction, in neutral bulk solution, are blocked by hydroxyl ions (or bicarbonate ions, doubtless present to a small extent in the water). Such ions would be stripped from the surface at bulk solution pH values less than 5—6.

The results for adsorption from sulphuric acid solution again indicate that chemisorption is not operative. Equilibrium is reached rapidly and the extent of adsorption, probably involving merely van der Waals type interaction, is similar to that from potassium chloride solutions. It may be pointed out that gold sulphate and complex auric sulphates are not known.

The adsorption results presented here may be considered in the light of appropriate electrokinetic data. Electrophoretic measurements [13] on gold in solutions of hydrochloric acid and potassium chloride show that the gold surface possesses a net negative charge.

TABLE 1. *Gold–potassium chloride solution.**

Bulk concn. (N)	σ_2 (e.s.u./cm.^{2})	ζ (mv)	$10^{-11}n^D_{K^+}$	$10^{-11}n^D_{Cl'}$	$10^{-13}\alpha_{K^+} = \alpha_{Cl^+}$	$10^{-11}\sigma_2/e$
2×10^{-5}	165	47	2·44	−1·00	1·79	3·43
5×10^{-5}	232	43	3·39	−1·48	2·59	4·85
1×10^{-4}	294	39	4·14	−1·95	3·07	6·10
2×10^{-4}	336	34	4·54	−2·46	3·64	7·00
5×10^{-4}	446	27	5·77	−3·40	4·49	9·21
1×10^{-3}	549	24	7·00	−4·38	5·26	11·41

TABLE 2. *Gold–hydrochloric acid solution.**

Bulk concn. (N)	σ_2 (e.s.u./cm.^{2})	ζ (mv)	$10^{-11}n^D_{H^+}$	$10^{-11}n^D_{Cl'}$	$10^{-13}\alpha_{H^+} = \alpha_{Cl}$	$10^{-11}\sigma_2/e$
2×10^{-5}	74	23	0·94	−0·60	3·6	1·54
5×10^{-5}	91	19	1·13	−0·79	7·3	1·90
1×10^{-4}	106	15	1·26	−0·94	11·0	2·20
2×10^{-4}	116	12	1·31	−1·10	15·1	2·40
5×10^{-4}	105	7	1·17	−1·03	21·0	2·19
1×10^{-3}	94	4	1·02	−0·94	26·8	1·96

* Values in the last four columns of each set are in terms of ions/cm.^{2}.

The data are reproduced in Tables 1 and 2 together with the present adsorption data. In these tables the charge density, σ_2, represents a net charge per cm.^{2} of the ionic layer on the solution side of the slipping plane, calculated by using the equation

$$\sigma_2 = (2n_B\varepsilon \boldsymbol{k}T/\pi)^{\frac{1}{2}} \sinh \boldsymbol{e}\zeta/2\boldsymbol{k}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n_B = number of ions per cm.^{3} of each sign in the bulk solution, far from the surface, ε = dielectric constant of the solution, $\boldsymbol{e}$ = the electronic charge, $\boldsymbol{k}$ = Boltzmann's constant, T = absolute temperature, and ζ = electrokinetic potential calculated from the experimentally determined electrophoretic velocity. A Gouy diffuse ion distribution is thus assumed in this layer.

The corresponding excess numbers of ions per cm.^{2}, n^D_i, in the layer are also given, as calculated from the equation [14]

$$n^D_i = -2\lambda n^B_i[1 - \exp(Z_i\boldsymbol{e}\zeta/2\boldsymbol{k}T)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where λ = equivalent double layer thickness, Z_i = ionic valency.

By comparison of $\sigma_2/\boldsymbol{e}$ with α, the total numbers of ions adsorbed per cm.^{2} of interface, it is apparent that the extent of adsorption is much greater than that which would explain the electrokinetic charge on the basis of anion adsorption into the region on the surface side of the slipping plane. It is then evident that considerable cation adsorption must occur in this region. In fact, the extent of cation adsorption on the solution side of the slipping plane is only *ca.* 1% of that on the surface side. If the electrokinetic slipping plane

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[13] Harrison and Elton, *J.*, 1959, 3838.

[14] Grahame, *Chem. Rev.*, 1947, **41**, 441.

corresponds at all closely to the boundary between fixed and diffuse layers of the Stern[15] model of the electrical double layer, then the net charge of the fixed layer must be determined by a small excess of anions relative to the total number adsorbed. Otherwise the slipping plane must be situated considerably further from the physical surface, within the diffuse layer.

Attempts to interpret an adsorption process by consideration of electrokinetic data alone[16] would thus seem somewhat ill-advised. This may be emphasised by noting that although the electrokinetic charge at the Au–KCl interface is considerably greater than that at the Au–HCl interface, the total adsorption of hydrogen chloride is some 3—5 times greater than that of potassium chloride at corresponding bulk solution concentrations.

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BATTERSEA COLLEGE OF TECHNOLOGY, S.W.11. [*Received, January 5th*, 1960.]

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[15] Stern, *Z. Elecktrochem.*, 1924, **30**, 508.

[16] *E.g.*, O'Connor, *Trans. Faraday Soc.*, 1956, **52**, 397; Anderson, Proc. 2nd Internat. Congr. on Surface Activity, 1957, Vol. III, p. 67.