Precipitation of Hydrolysis Products on to Oxide Surfaces*

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Several complex physico-chemical phenomena occur when oxide surfaces are brought into contact with solutions of hydrolysable salts. Both the hydrolysis and the surface chemistry of the oxide are pH dependent, and by appropriate variation of pH the adsorption of solution species at the surface may be controlled to bring about such effects as charge reversal and coagulation of the oxide particles, growth of a new phase at the surface, etc., many of which have technological significance.

The surface chemistry of an oxide surface in contact with an aqueous solution is determined to a large extent by the dissociation of the surface hydroxyl groups. We may conveniently write the equilibria as

$$M-OH_2^+ \rightleftharpoons M-OH \rightleftharpoons M-O^- + H^+$$

$$\leftarrow \text{decreasing pH} \qquad \text{increasing pH} \rightarrow$$

which indicates that by appropriate adjustment of pH the surface groups may carry either a positive or negative charge, while at an intermediate value they are undissociated. This latter pH is the point of zero charge (pzc) of the oxide and more truly represents a net zero charge on the surface. The pH at the pzc has a specific value for each oxide depending on the electronic character of the metal-oxygen bond and the degree of stoichiometry of the surface. Parks[1] has reviewed the pzc values for oxides — typical values are SiO_2 pH 1—2, TiO_2 pH 5—6, Al_2O_3 pH 8—9, the range of pH indicating variations between samples. Microelectrophoresis provides a useful tool for establishing the pH at which the oxide particles do not move in an electric field — called the iosoelectric point (iep), and is equal to the pzc when no specific adsorption of other ions from solution occurs in the innermost region of the electric double layer associated with the particles. This technique has already proved valuable in studies of the behaviour of oxides in solutions containing hydrolysable species e. g. it may be used to directly observe charge reversal on adsorption, and where a new hydrated oxide is precipitated on to the oxide substrate the chemical character of the coated surface may be defined by studying the electrophoretic behaviour, with particular reference to the isoelectric point.

The hydrolysis of metal ions in solution may in general be represented by

$$M^{n+} + 2 H_2O \rightleftharpoons M(OH)_2^{(n-2)+} + 2 H^+$$

and the fraction of total metal present as each hydrolysis species is strongly pH dependent. Hydrolysis diagrams, in which the concentration of ionic species

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in solution in equilibrium with the solid hydrated oxide is plotted against pH, are well known (e. g. $Al(OH)_3$, ref. 2) — they are often complex and not always accurately defined because of the difficulties associated with analysis of the numerous species that exist in such solutions. The silica system is a good example of a less precise hydrolysis diagram — perhaps the alumina system is more accurately defined although minor variations exist from one crystal form to another.

So when an oxide surface is brought into contact with a solution containing a hydrolysable salt, since the chemical behaviour of both phases are pH dependent, it is not surprising that some very complex phenomena are observed. Adsorption of the various solution species occurs at the oxide surface, and this may cause charge reversal which also give rise to coagulation. Furthermore sufficient species may adsorb and nucleate a new surface phase from which a coating is derived with a new »oxide« surface. Such phenomena have technological significance such as in mineral flotation, water clarification, catalyst and pigment preparation etc. We shall discuss certain effects which have been observed with dispersions of colloidal oxide particles in solutions of complex salts, referring particularly to the creation of new surface phases.

It is frequently observed[3,4] that there is an abrupt increase in adsorption at the combination of total metal ion concentration and pH corresponding to the formation of the first hydrolysis product, and the increase is usually from a few % to almost 100% over a very narrow pH range (about 1 unit). For example on a SiO_2 surface the adsorption of Fe (III) increases abruptly at pH 2.2 and of Cr (III) at pH 4.1, both values corresponding to the onset of hydrolysis[5]. Numerous examples of this occur with multivalent ions, and for these it seems that the hydrolysis products are more surface active than the unhydrolysed species. However, this generalisation does not appear to be applicable for many divalent ions e. g. for the Co (II) system it has been clearly demonstrated that the adsorption on SiO_2, which rises steeply over a narrow pH range is not simply related to the formation of the first hydrolysis product $CoOH^+$, nor just to the specific adsorption of the Co (II) ion on the surface. James and Healy[6] have interpreted the adsorption behaviour in this and similar systems in terms of the relative magnitude of coulombic and solvation energy changes with pH — the change in surface charge with pH is reflected in the coulombic term.

Another common observation[7,8] is that for many ions, particularly those which hydrolyse strongly, there is a reversal in the charge of the negative oxide surface (above the pzc) with increase in pH followed by a further reversal at higher pH, and these changes occur as a result of adsorption. (For surfaces below the pzc a further charge reversal occurs on increasing pH, corresponding to the pzc of the oxide). These effects are readily observed by microelectrophoresis, and are related to the coagulation behaviour associated with systems containing complex ions for which domains of coagulation and stabilisation exist in the concentration versus pH plots. For the SiO_2/Co (II) system James and Healy[9] show that the two charge reversals above the pzc occur at pH values in the region of 8—9 and 9.5—10.5 respectively, the precise value depending on the SiO_2 concentration. Their explanation is that the electric field of the surface induces precipitation of the metal hydroxide at pH values lower than those corresponding to bulk precipitaion. At intermediate pH the

charge reversal corresponds to surface nucleation of the hydroxide, thus a surface coating is formed and if completely covering the surface the charge reversal at high pH corresponds to the pzc of this metal hydroxide layer. Furthermore it would seem that metal hydroxide precipitated on a silica surface behaves in a similar manner electrochemically to that of a normally precipitated hydroxide. Hence for a series of mixtures of increasing Co (II) concentration the electrophoretic mobility *versus* pH curves change from that characteristic of pure silica, through complex plots showing two charge reversals until at high concentrations when the SiO_2 surface is completely coated, the curve is characteristic of that of pure cobalt hydroxide. Useful information on the precipitation of one »oxide« on the surface of another is therefore obtainable from microelectrophoretic data. Several systems [SiO_2 and TiO_2 with Co (II), Ca (III) and Th (IV)] were studied by James and Healy[9], and they point out that the phenomenon is quite common with surfaces in contact with solutions containing hydrolysable ions.

For durability of paint films containing titanium dioxide pigments it is practice to coat the surface of the oxide particles with a layer of another oxide or mixed oxide to reduce the catalytic effect of the reactive titanium dioxide on the decomposition of the paint medium during exposure to sunlight[10]. The mechanism of weathering of paint films is subject to considerable debate, a situation exacerbated by the difficulties of measuring the durability effect, as well as by the complexity of the mechanism of coating the oxide surface and of assessing the physical and chemical characteristics of the coating formed. One obvious requirement is that the surface of the titanium dioxide is completely covered, and with a sufficiently thick coating that its surface chemistry is not affected by the substrate. Penetration of molecular and atomic species through the coating is related to its porosity and chemical character, and therefore both these factors are also relevant to durability. Microelectrophoresis provides one means of establishing the nature of the coating surface, and coupled with electron micrographs, vapour adsorption and X-ray diffraction it is possible to achieve a fair understanding of the coating mechanism.

Use of the microelectrophoresis technique is admirably illustrated by the following experiment. A slurry of titanium dioxide (200 gpl) at pH 3 was prepared and aluminium sulphate solution added. At this pH there was present no solid phase containing aluminium. The system is then neutralised by slow addition of caustic soda, and samples taken at various pH values for microelectrophoretic examination. On increasing the pH at constant total Al (III) concentration the hydrolysis limit in the region of pH 4 is crossed and some basic aluminium sulphate is precipitated on to the titanium dioxide surface. Samples were withdrawn at pH 3.5, 3.8, 4.0 and 4.6, which were then filtered, washed with dilute sulphuric acid (at the same pH), and dried. Then redispersed for electrophoretic mobility measurements, shown in Fig. 1, which demonstrate the progressive change from the mixed surface of TiO_2 and $Al(OH)_3$ with three charge reversals (first the isoelectric point of TiO_2, the second due to precipitation on the surface and the third the isoelectric point of $Al(OH)_3$), to the surface completely coated with $Al(OH)_3$ at pH 4.6. At this point the slurry was filtered, washed with dilute acid, and then reslurried to pH 4.6. Sodium silicate solution was added following which the pH naturally rises — samples were taken at pH 6.1 and 8.5, and the microelectrophoretic
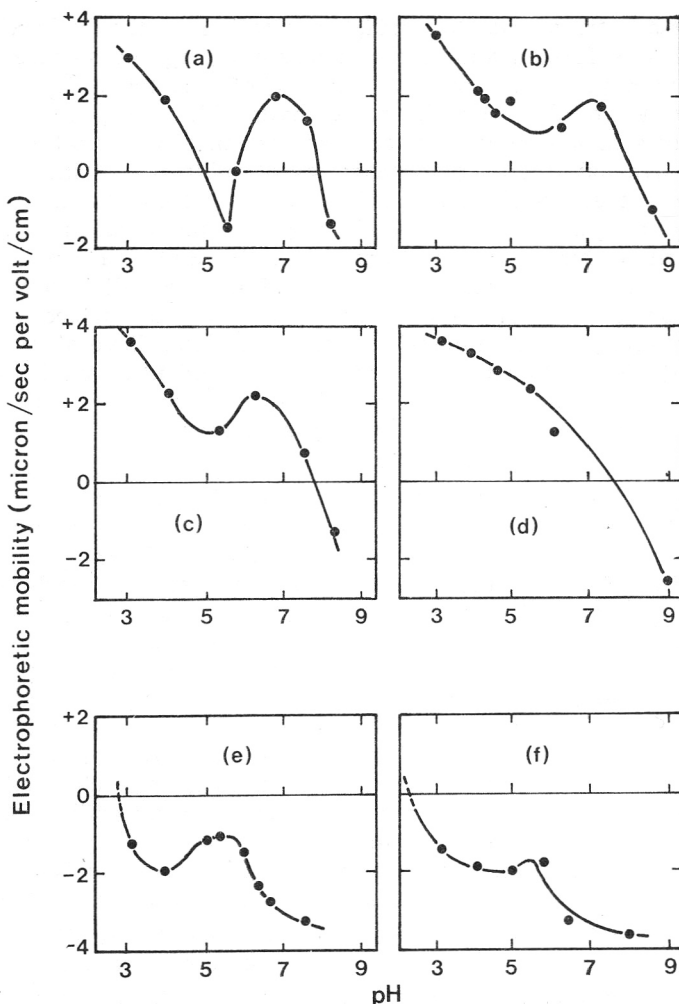
Fig. 1. Electrophoretic mobility of samples taken at various stages in the precipitation of alu-
minium hydroxide on a rutile surface followed by hydrous silica. Samples removed from the
coating system at (a) pH 3.5, (b) pH 3.8, (c) pH 4.0, (d) pH 4.6, (e) pH 6.1, (f) pH 8.5.

data demonstrate the precipitation of polysilicic acid on the $Al(OH)_3$. Although
all the silicon added was precipitated on the oxide particles, the electrophoretic
mobilities do not reflect a fully coated »hydrated silica« surface. Certainly the
curve for the pH 8.5 sample is very similar to those well established for silica
in that it has an (extrapolated) isoelectric point in the region of pH 2, but the
inflection at ~ pH 5 suggests that some of the underlying $Al(OH)_3$ is showing
through.

It would appear that the electrochemical properties of a surface coating
are to a first approximation independent of the method by which preci-
pitation occurred. Hence one might expect the electrophoretic behaviour
of an oxide completely covered with hydrated silica to be same whether the
silica coating was formed by nucleation and growth on the substrate $(TiO_2$

surface, or by coagulation on to the surface of silica particles formed in the liquid phase. Furthermore either system would have identical electrophoretic properties to that of the normally precipitated hydrous silica, and there is quite a lot of evidence to support this view.

However, the different physical character of the two types of coating has been clearly demonstrated, and the differences are significant to pigment properties. A common technique for depositing hydrous silica on titania is to add sodium silicate solution to pigment slurry, digest at 60^0 C for half an hour, and then reduce the pH to 7.0 with sulphuric acid, followed by filtration, washing and drying. Under these conditions silica particles ($\sim$ 40 Å diameter) are formed in suspension and deposited on the titanium dioxide surface (the deposition is more effective when Al (III) ions are present). The surface area of the coated titania is much higher than that of the substrate, but the nitrogen adsorption isotherm shows no hysteresis $i. e.$ there are no pores of the macro or meso-type, suggesting that the deposit is made up of coagulated silica particles. Heats of immersion in water for samples containing increasing amounts of silica at the surface are given in Table I. The surface areas of the samples (Table I) when plotted against $\%$ SiO_2, are linear with a slope of 700 m²/gm which corresponds to spheres of average diameter 40 Å.

TABLE I

Silica Coated Rutile

$\%$ SiO_2	Surface Area (N_2) (m²/gm)	Heat of immersion (ergs/cm²)
0	7.0	700
1.27	11.2	370
3.95	31.3	245
8.57	62.3	180

The immersional heats at zero and 8.57% SiO_2 reflect the values for the pure oxides, with the intermediate values corresponding to a mixed surface.

To obtain a coherent coating of hydrous silica on titania by a nucleation/ /growth mechanism, it is necessary to carefully control the addition of reagents and the pH changes. By slow and uniform addition of sodium silicate solution and dilute sulphuric acid to a slurry of base rutile, maintaining the pH at 9, a more uniform and compact coating is obtained as revealed by electron microscopy. Zettlemoyer et al.[11] have measured nitrogen and water vapour adsorption on silica coated rutiles prepared in this manner and containing increasing proportions of silica, as well as the heats of immersion of the samples in water. They conclude that the silica surfaces produced by this method are non-porous to nitrogen but porous to water vapour, a significant fact for the durability of the rutile. Table II gives the relevant data taken from their paper. The high heats are somewhat surprising, particularly for the pure TiO_2 [600—700 ergs/cm² is the usual value], and the heavily coated surface [expect a value about 200 ergs/cm², as for pure silica]. They probably reflect an uncertainty in the water areas for the porous surface. Nevertheless the trend is significant.

TABLE II

Silica Coated Rutile

% SiO_2	Surface Area (N_2) (m^2/gm)	Surface Area (H_2O) (m^2/gm)	Heat of immersion (ergs/cm^2 based on H_2O area)
0	6.1	3.35	1070
2	7.6	6.1	740
5	8.1	9.35	580
10	8.25	16.25	505
15	8.0	18.1	485

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IZVOD

Taloženje produkata hidrolize na oksidne površine

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Opisan je niz fizičko-kemijskih fenomena, koji nastaju kada se neka oksidna površina dovede u kontakt s produktima hidrolize. S obzirom da i hidroliza, a i površinska svojstva oksida ovise o pH, kontrolom pH otopine moguće je postići efekte poput promjene predznaka naboja, koagulacije, rasta nove faze na površini, kao i nekih modifikacija katalitičke aktivnosti i stabilnosti pigmenata u tehničkim premazima. Navedeni su primjeri promjene elektroforetske gibljivosti rutila prekrivenog s $Al(OH)_3$ i topline kvašenja površina rutila s različitim sadržajem SiO_2.

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