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Hydrous zirconium dioxide: interfacial properties, the formation of monodisperse spherical particles, and its crystallization at high temperatures

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The characteristics of hydrous zirconia gels obtained by hydrolysis of highly acidic $ZrOCl_2 \cdot 8H_2O$ solutions at $\sim 100^\circ$ C are described. Under adequate conditions, monodisperse spherical hydrous zirconia is obtained. The role of sulphate and chloride ions is described. The gel has a large water content, indicating only modest crosslinking. Crystallization upon heating takes place with the formation of both monoclinic and tetragonal zirconia polymorphs; X-ray line widening studies do not indicate a particle size–crystal structure correlation. On the basis of this observation and using Stranki's rule, the crystallization sequence upon heating is rationalized. Surface properties of hydrous zirconia are discussed on the basis of electrophoretic measurements, and compared with those of baddeleyte. The site binding model is not very adequate to describe these systems, and the existence of a very thin gel-like region at the baddeleyte–water interface is postulated.

1. Introduction

Because of their wide use in high temperature ceramics and their electrical conductivity at high temperature, zirconia and zirconia doped with various metal oxides have been widely studied from the structural point of view. In our case, interest in this material arises because of its presence as the corrosion product of zirconium-based alloys (such as Zircaloy) on the fuel element cladding in nuclear power reactors. The oxide on the fuel element cladding surface interacts with colloidal particles of corrosion products (iron oxides), carried by the circulating coolant. Depending upon double layer properties of both cladding and particles, these may be deposited on the fuel elements [1, 2]. Deposition on the fuel element surface is one of the crucial points in the mechanism of formation of ^{60}Co and many other radionuclides; this is especially true in all-Zircaloy cores, such as those of the Canadian CANDU reactors [3, 4], but it may also be significant in other reactors where contribution from other core structural components is important or even dominant [5]. Previous work from our laboratory [1, 2] and from others [6, 7] has shown evidence for the importance of

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ζ-potential in determining the deposition coefficient of corrosion products of colloidal particles on the fuel elements, and values of ζ obtained for baddeleyte in aqueous suspensions [8] have been used to model the clad–particle interactions. The structure of zirconium oxide grown on to zirconium alloys has been widely studied, especially by Ploc [9–13] who has shown that this material is a complex mixture of the tetragonal and cubic polymorphs, as well as intermediate stages, which undergo a dynamic process of nucleation, recrystallization and growth. Therefore, we considered it of interest to extend the measurements of ζ-potentials previously carried out on baddeleyte [7], and in the present work we report electrokinetic mobility data for hydrous zirconium dioxide, together with a new procedure to prepare this material; under adequate conditions monodispersed spherical hydrous zirconia could be obtained, thus providing an important preparative procedure for all types of study on the colloidal properties of hydrous zirconia.

This material is also of interest because of its ion exchange properties [14–16]; thus, large amounts of chloride and other anions are sorbed by hydrous zirconia [14]. Hydrous zirconia is a gel-like material, and as such it is not expected to behave according to the site-binding model [17–20] in its surface properties. We have reported that baddeleyte is accommodated with difficulty only within the frame of this model, and it was suggested that a gel-like surface layer may also be important in the case of the crystalline material [8]. It was considered of interest, therefore, to compare the surface properties of baddeleyte (reported previously) with those of the hydrous zirconia (reported here), in order to establish the extent of similarities in their behaviour.

Finally, we have explored the crystallization of our hydrous zirconia by heating, in view of the growing importance of the so-called "gel route to ceramics" [21, 22]. It is well known that the metastable tetragonal polymorph can be prepared by low temperature (~ 300° C) heating of the hydrous oxide [22–31]. There is still debate on Garvie's assumption that the tetragonal polymorph is formed as a crystal size effect [25, 26]. Thus, Murase and Kato [30] showed no relationship between crystallite size and crystal structure, and Mitsuhashi *et al.* [27] and others [32, 33] proposed a rationalization of their observations on the basis of a martensitic transformation; on the other hand, Bailey *et al.* [34] showed that monoclinic zirconia reverted to the tetragonal variety upon ball milling, and both Whitney [35] and Cypres *et al.* [36] have pointed out the importance of impurities. Because our material was prepared under different conditions and in view of the above controversy, X-ray line broadenings of the most characteristic lines of both the tetragonal and the monoclinic varieties formed upon calcination were measured, and the results used to propose a general view of the polymorphism of zirconia at low and moderate temperatures (up to 800° C).

2. Experimental details

2.1. Preparation of hydrous zirconium dioxide

Reagent grade $ZrOCl_2 \cdot 8H_2O$, K_2SO_4 and HCl were used to prepare stock solutions (0.1, 0.1 and 2.4 mol dm^{-3}, respectively). These solutions were filtered through 0.1 μm pore polycarbonate membranes and then mixed in adequate ratios in glass ampoules which were sealed under flame and kept at constant temperature to ± 1° C in an oven. A large number of experiments were carried out varying concentration, temperature and time of ageing as indicated in Table I, and the solid phases thus obtained were repeatedly washed with doubly distilled water (until constant pH) and filtered.

2.2. Characterization of particles

The morphology of particles was examined by transmission electron microscopy (TEM) in a Phillips EM 300 microscope and by scanning electron microscopy (SEM) in a Jeol 35-S apparatus. The particles were resuspended in water and, for TEM observations, deposited on collodion-coated grids and further evaporated; for SEM observations, some droplets of particle-containing water were evaporated onto glass plates stuck on aluminium studs and coated with gold.

Thermogravimetric studies were carried out in a Cahn 1000 electrobalance with a Stanton Redcroft oven and temperature programmer. The crystallization behaviour of calcinated samples was followed by X-ray diffraction using the Debye Scherrer method and Ni-filtered Cu radiation of a Phillips generator type PW 1140/

TABLE I Morphological characteristics of amorphous zirconia particles obtained at a constant sulphate : zirconium ratio of 2*

Sample	Zr/M ($\times 10^2$)	HCl (M)	T (K)	Ageing time (d)	Particle size (μm)	Particle size, scatter
1	4.6	0.8	338	1	0.1–2.0	large
2	4.6	1.0	338	2	0.1–2.0	large
3	1.0	0.0	343	1	0.3	large
4	1.0	0.5	358	1	0.2–2.0	large
5	1.0	0.8	358	2	0.1–1.0	large
6	1.0	1.0	358	3	0.2–0.5	large
7	1.0	1.0	371	4	0.7–1.5	large
8	0.5	1.2	371	8	0.8	small
9	0.5	1.0	371	12	0.8	very small

*At lower sulphate : zirconium ratios the scatter in particle size was large in all cases and the morphology was not spherical.

90. Peak intensities of the (1 1 1) line of tetragonal ZrO_2, the (1 1 1) line of monoclinic ZrO_2 and the (1 1 0) line of crystalline α-quartz standard (average size particle: 37 μm) were measured with a Joyce-Loebl microdensitometer. The average crystallite sizes were calculated from the breadth at half peak height using the Scherrer formula [37] corrected for instrumental broadening.

Electrokinetic measurements were performed in a Zeiss Cytopherometer according to techniques describes previously [8] and ζ-potentials were calculated from the data using a computer program developed by O'Brien and White [38] based on the procedure described by Wiersema *et al.* [39].

3. Results

3.1. The formation of monodisperse hydrous zirconia

The usual procedure for preparing hydrous zirconia involves the hydrolysis under alkaline or neutral conditions [14, 15, 21, 22, 24, 40]. Under these conditions it is impossible to control the local chemistry, and different, irreversible processes take place simultaneously. The importance of local pH fluctuations during base addition has been pointed out by Dousma and de Bruyn for the case of iron hydrous oxide formation [41–43]. We have circumvented this difficulty by taking advantage of thermally enhanced hydrolysis of Zr(IV) in strongly acidic solutions to generate the gel slowly and under very precise conditions. This is a modification of the preparation described by Johnson and Kraus [44], Clearfield [45] and Murase and Kato [46].

X-ray diffraction shows that the material obtained by hydrothermal ageing of strongly acidic solutions is, as expected, amorphous. No crystallization takes place under quiescent ageing, as compared with the formation of baddeleyte upon refluxing the boiling suspension [47]. Even when no crystallization takes place, boiling solutions are not adequate for the obtention of monodisperse material, see e.g. [46]. Chemical analyses indicate that the unwashed solid phase obtained by filtering through submicronic polycarbonate membranes contains high amounts of hydrochloric acid, of the order of 30%. Repeated washing of the solid, or neutralization in alkaline solution can yield the acid-free material. This washed solid still contains large quantities of entrapped water, as shown thermogravimetrically. The 43% w/w is accounted for by loosely bound water, which is released up to ~ 320° C, and a further 13% w/w corresponds to tenaciously held water*; these figures are higher than those corresponding to the hydrolysis in more alkaline solutions [29, 40].

It is seen that the material prepared by forced thermal hydrolysis is especially suited to use as an ion exchanger, and furthermore, as it is possible to prepare samples of spherical particles with a very narrow particle size distribution (see below), it is also very adequate for fundamental studies.

Scanning electron micrographs show that the usual particle size is 1 to 2 μm diameter, the shape being essentially spherical. Typical micro-

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*These figures may include a small contribution from trapped hydrochloric acid.

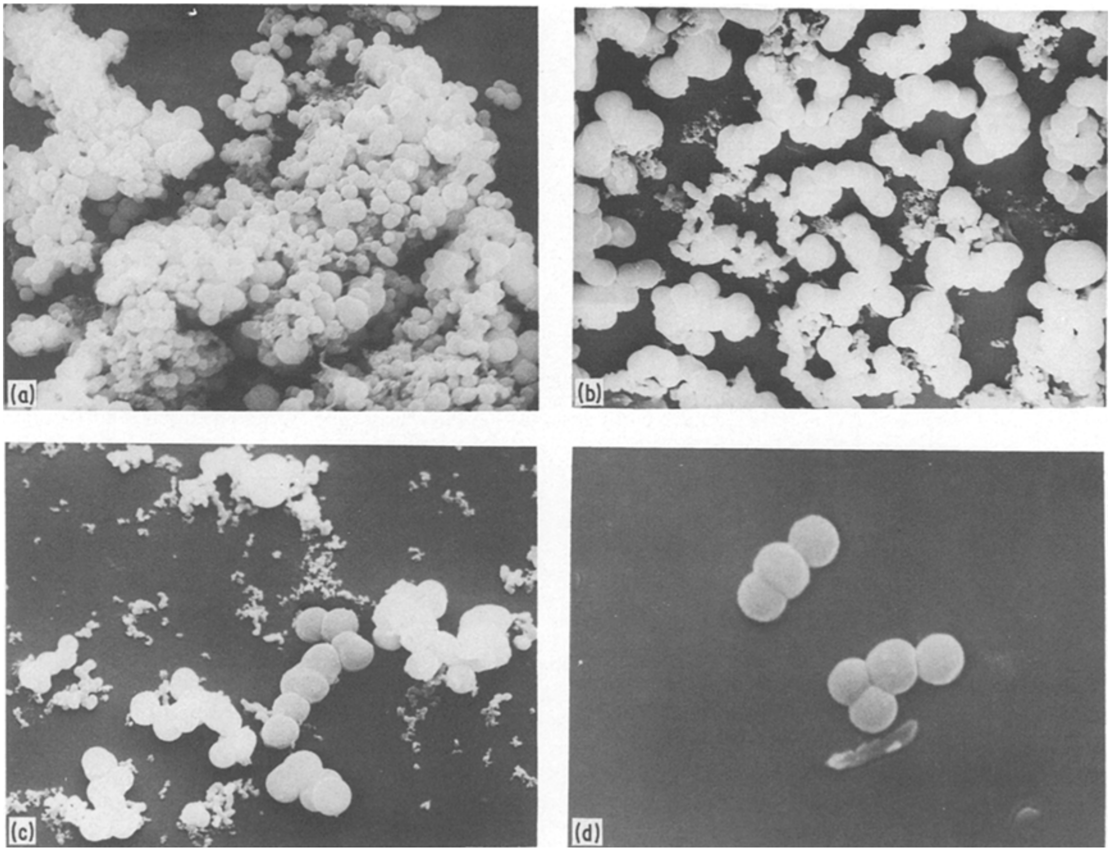

Figure 1 (a) to (d) Scanning electron micrographs of hydrous zirconium dioxide corresponding to cases 2, 6, 7 and 9 of Table II, respectively. Horizontal bar is 10 μm in (a), (b) and (c), and 1 μm in (d).

graphs are shown in Figs. 1a to d. The size dispersion was variable as seen in Table I, and critically dependent on experimental conditions. In general, the shape is not very regular for gels obtained in hydrochloric solutions free of sulphate, and becomes spherical upon addition of K_2SO_4. At the lowest zirconium concentration used, maintaining a constant sulphate to zirconium ratio $R = 2$ (Table I), the material becomes monodisperse. The effect of added sulphate ions is not a peculiar feature of this system. Monodisperse chromium(III) oxide has also been prepared by thermal hydrolysis at high temperature in the presence of sulphate [48, 49]. The role of sulphate has been shown to be the generation of sulphato-complexes which act as precursors; these are the only species which aggregate to yield particles. In the case of Cr(III), sulphate ions are released at a later stage, and thus the solid does not contain measurable amounts of sulphate [48, 49]. In the case of $ZrO_2 \cdot H_2O$, it is well known that sulphate is adsorbed less strongly than chloride [14]; consequently, sulphate removal from its complexes is also probably involved in the polymerization mechanism. Chloride, on the other hand, is not easily replaced and it is present in the final product unless very strong rinsing is used [14]. Matijevic [50] has proposed several general methods of preparing monodisperse colloidal particles of hydrous metal oxides, including the controlled thermally enhanced hydrolysis of metal cations in acidic solutions [47]. Hydrolysis slowly releases the "precursor complexes" into solution; in a first stage these slowly condensate until they eventually generate nuclei. Once the nuclei burst has taken place, oversaturation decreases below the nuclei-forming threshold. At this stage particle growth only removes the additional precursor complexes at a rate kinetically controlled by the rate of their formation. Ostwald ripening and growth characteristics take care of any original polydispersity as described by Overbeek [51]. In our system such conditions could be achieved by ageing a solution 5×10^{-3} M in ZrO_2Cl_2, 1 M in HCl and 5×10^{-3} M in K_2SO_4.

Both in solid zirconyl chloride and in its aqueous solutions, zirconium is present mainly as the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ which contains zirconium(IV) bound to four bridging OH ions and to four water molecules [52]. The solutions of this species are known to polymerize irreversibly, especially upon heating [44]. The aggregation of the tetramers yield naturally the hydrous material, which has also been shown to contain tetrameric units linked by hydroxo and/or oxo bridges [53, 54]. Gimblett *et al.* [24, 40] have shown that the oxolation and olation processes responsible for condensation are strongly pH dependent. Thus, under our experimental conditions, only modest crosslinking is expected, different Zr_4 polyhedra sharing only –OH– bridges. The monodisperse material is formed under the mildest conditions, i.e. high acidity and low temperature, both factors favouring a very low degree of crosslinking and high water content. This is not appreciably changed by immersion in alkaline solution, which brings about only ion exchange with release of sorbed HCl.

In order to explain the similarities and differences in the effect of sulphate on the formation of chromium(III) and zirconium(IV) hydrous oxides, it must be accepted that both the nucleation and the growth stages are influenced by sulphate. In the case of chromium(III), no nucleation takes place if sulphate (or phosphate) is not present [48, 49] whilst hydrous zirconia is also formed in sulphate-free chloride solutions, probably because the original tetrameric species are close enough to the critical nucleus size (see [53–55], and Zr(IV) is not as inert kinetically as Cr(III) for hydrolytic reactions, even though our experiments were carried out at much lower pH values. The lack of nucleation in the chromium system when sulphate-free, renders this system better suited to adequately control and separate nucleation and growth. The influence of sulphate is by no means unique; it has been shown that other potential ligands present in the original solution (including CO_2 and NH_3) greatly influence the thermal evolution of the gel microstructure [56].

Matijevic *et al.* [57] obtained highly monodisperse particles of TiO_2 through the hydrolysis of $TiCl_4$ in very acidic solutions; both polymorphs (anatase and rutile) are found under certain conditions. This case is an actual crystallization process, whereby hydrolysis of $TiCl_6^{2-}$ slowly yields monomeric Ti(IV) ions able to form crystalline nuclei. We have attempted a similar procedure, i.e. the forced hydrolysis of potassium hexafluorozirconate(IV) solutions. ZrF_6^{2-} is known to be extremely stable, the Zr–F bond energy being $\sim 147\,\mathrm{kcal\,mol^{-1}}$ [58]. Thus, extreme conditions are required to hydrolyse this species, and the material obtained is neither crystalline to X-rays, nor monodisperse.

3.2. Phase transformations

It is well known that upon calcination, $ZrO_2 \cdot xH_2O$ gels loose water at 230° C without a noticable increase in their crystalline character. At $\sim 400°$ C, tetragonal ZrO_2 crystallizes exothermically as previously reported by other authors ([24] and references therein). The formation of the metastable tetragonal phase has

TABLE II Zr–X distances in zirconyl chloride, hydrous and tetragonal zirconia

Zr–X	$ZrOCl_2 \cdot 8H_2O(s)$*	$ZrO_2 \cdot xH_2O$ (am)†	ZrO_2 (tetr)‡
Zr–O (coord)	2.1		
	2.2	2.2	2.1
	2.3		2.4
Zr–Zr	3.6	3.5	3.3
		3.7	3.7
Zr–O (distal)	4.0–4.4 4.7–4.9	4.7	4.2
Zr–Zr (coplanar)	5.8	6.0	6.0

*Calculated from [58].
†Calculated from [53].
‡Calculated from [59].

TABLE III Scheme of ZrO_2 phase transformations

t (° C)	Species	Process
	$[Zr_4(HO)_8(H_2O)_{16}]^{8+}$ (aq)	
100	↓	Precipitation
	$[Zr_4O_{8-x}(OH)_{2x} \cdot yH_2O]_n$ (gel)	
100–300	↓	Drying
	$Zr_4O_{8-x}(OH)_{2x}$ (dried gel)	
400	↓	Glow crystallization
	ZrO_2 (tetr)	
400–900	↓	Martensitic transformation or dissolution recrystallization
	ZrO_2 (monoclinic)	

been rationalized in terms of a favourable contribution of surface energy, which should predominate in very small crystallites [25, 26]. There is a close structural relationship between the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ [59], the hydrous oxide [53], and the tetragonal polymorph [60]. This is borne out by the similarities between Zr–Zr and Zr–O distances in the three species, see Table II. It is a well known phenomenon that the tetragonal polymorph should therefore: (a) form first, and (b) be stabilized in small particles because of favourable surface energy considerations (Ostwald–Lussac rule) [61]; it is impossible to distinguish between purely kinetic factors and thermodynamics as the reason for tetragonal phase formation. Also note that the formation of the tetragonal variety is in line with Stranski's rule that phases appear in a sequence given by their ease of nucleation [62]. A logical comprehensive pathway from zirconyl chloride solutions to ZrO_2(cryst) would be shown in the scheme shown in Table III. This scheme takes into account the results of Vivien *et al.* [23], who have shown that the amorphous state can be considered as intermediate between the true solution and the crystallized oxide. Furthermore, Crucean and Rand [29] have demonstrated that the more hydrated gel precipitated at lower pH values gives higher yields of the tetragonal variety; the above scheme is in agreement with this fact and with the proposed explanation based on the strains required to crystallize the hydrous oxide. The crystallization of amorphous zirconia to yield the tetragonal polymorph is known to take place in a rather strain-free fashion in hydrothermal conditions [63]; a topotactic crystallization on amorphous nuclei has been proposed for this process[†].

The transformation of the tetragonal crystallites into the monoclinic ones is essentially controlled by kinetic factors; in dry conditions like ours, it is probably a martensitic transformation [27, 32, 33]; its rate can, however, be affected by other factors. Thus, in hydrothermal media dissolution–recrystallization may take place[‡]; this explains the role of water vapour on the kinetics of this transformation [30]. Note also that evaporation–condensation has been reported to play an important role in the sintering of zirconia [65]. Proof of the metastability of tetragonal zirconia, even in very small crystallite size, was given by Tani *et al.* [64] who prepared ultrafine baddeleyte (20 nm in size) in hydrothermal conditions.

Upon heating our material to 550° C, crystallization is observable by the appearance of the diffraction lines characteristic of both polymorphs. Crystallite and particle size were compared from X-ray line widths and scanning electron micrographs. Each particle is the aggregate of a large number of very small crystallites. The average size of tetragonal zirconia crystals obtained at 500° C is 7.4 ± 0.4 nm, very similar to the corresponding value for baddeleyte (6.6 ± 0.4 nm)[§]. At higher temperatures, the crystal sizes are larger, and at 820° C they are close to the limit of applicability of the X-ray line broadening method. In every case the crystallite size of both polymorphs are similar, in agreement with Crucean and Rand [29] (cf., however [34]), whilst the relative abundance is controlled both by calcination time and temperature. These observations agree well with the results of Livage *et al.* [53] who reported that crystallites are formed on discrete nuclei of the original particle, the number of active nuclei increasing with temperature. We have observed,

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[†] According to Nishizawa *et al.* [28], a cubic polymorph may mediate between the amorphous state and the tetragonal crystallites.

[‡] Apparently, whether dissolution–recrystallization or direct solid-phase transformation take place, depends critically on the experimental conditions [28, 63, 64].

[§] These values are obtained using the correction for wide crystallite size distribution [37]. If a narrow size distribution is assumed, the resulting values are 5.6 ± 0.1 and 5.3 ± 0.1 nm, respectively.

however, that alkali-washed samples give rise to baddeleyte particles that are smaller than those of the tetragonal polymorph. This strange result has been reported previously by other authors [30] and tentatively assigned to twinning and strain fracture of baddeleyte crystals.

In the heating procedure baddeleyte is always the final product, indicating that surface energy considerations do not alter the relative thermodynamic stability of both phases in the whole temperature range (> 400° C) and particle sizes. The formation of tetragonal ZrO_2 by prolonged milling of baddeleyte might imply a thermodynamic stabilization of the tetragonal polymorph when the size is small enough, but most probably mechanical activation is responsible for the observed transformation [66].

3.3. Electrophoretic mobilities

Baddeleyte has been studied previously, both by us [8] and by others [67]. The isoelectric point (i.e.p.) has been found to be at $\text{pH} = 6.7$. There are also two reports in the literature on the electrophoretic mobilities of hydrous amorphous zirconia: both Mattson and Pugh [68] and Ray and Kahn [69] report an isoelectric point of ~ 7. These values seem to be much more reliable than earlier figures as different as 4 [70] and ~ 10.5 [14][¶]. There seems to be much more scatter in the reported values of the point of zero charge (p.z.c.), which is usually determined as the intersection point of acid–base titrations at various ionic strengths. Values ranging from 2.8 to 7.8 have been reported for the hydrous oxide and for baddeleyte [13, 69, 72–74].

In Fig. 2 we show the results for our amorphous hydrous oxide, which had been washed until no further chloride release was detected. The i.e.p. is located at lower pH values than the values reported by Mattson and Pugh, and Ray and Kahn. This is due to the difficulty of releasing all sorbed chloride; under our preparative conditions the original material is completely "soaked" in HCl, and this is released with much difficulty in the latter stages, affecting the electrophoretic mobilities, because these are very sensitive to minute amounts of chemisorbed ions. Using the Gouy–Chapman equation for the diffuse region of the double layer, the chloride surface excess at the i.e.p. can be calculated to be $6.3 \times 10^{-8}\ \mu\text{mol cm}^{-2}$.

It must be concluded that the i.e.p. of hydrous zirconia free of adsorbed ions is ~ 6.7 and is shifted to lower pH values by sorbed anions. The electrokinetic properties of amorphous and crystalline zirconia are therefore not very different. On the other hand, the sorptive properties of hydrous amorphous zirconia give rise to very high apparent surface charges when calculated from titration data [69]; when the pH-equilibration method is used to determine the p.z.c., the slow release of sorbed acid or base is responsible for a large scatter of values, and discrepancies with potentiometric technique data.

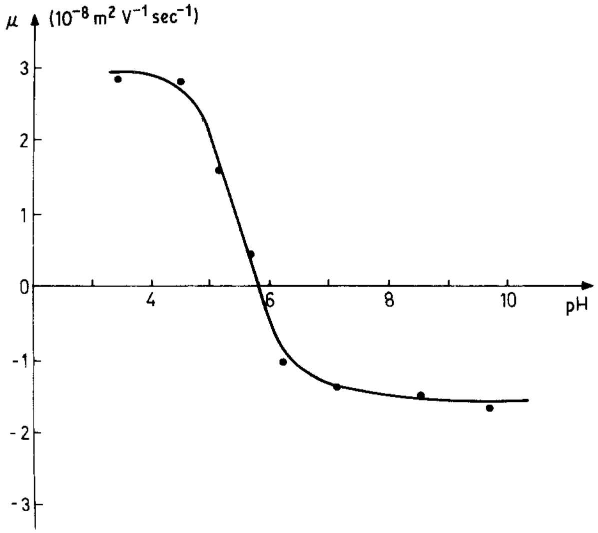

Figure 2 Electrophoretic mobility of hydrous zirconium dioxide as a function of pH, at 25° C, $I = 0.001\ \text{mol dm}^{-3}$ (KNO_3).

[¶] It is interesting that experimental values seem to be completely at variance with the value of 12 predicted on the basis of crystallographic data [71].

The gel-like structure of amorphous zirconia renders this material unsuitable for the site-binding treatment of surface electrification (cf. [72]). The difficult accommodation of baddeleyte to the site binding model has been pointed out previously. It seems probable that crystalline zirconia immersed in water undergoes surface modification to yield a thin gel-like coating. This explains among other facts, the relative lack of influence of ionic strength on the value of the surface charge developed on baddeleyte [8]. Such a layer must be, however, only a few monolayers thick, and as such the double layer in this case is better described as intermediate between those of crystalline and gelatinous oxides. It is therefore reasonable to use the data on baddeleyte to model colloidal interactions on fuel element surfaces, even though their oxide layer is complex in morphology and structure [9, 10].

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