Electrokinetic Behaviour and Interaction with Oxalic Acid of Different Hydrous Chromium(III) Oxides

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Three samples of hydrous chromium(III) oxide have been prepared by different procedures, and their electrokinetic mobilities have been measured. In mineral media, isoelectric points were found to be 8.45 ± 0.15. This value is shifted from the solution isoelectric point by -0.35 ± 0.15, due to the contribution of solvation energy to the energy of ionic adsorption. On the basis of a simple model, it is suggested that the two successive surface acidity constants of hydrous chromium(III) oxide are $pK^S_{a1} = 7.17$ and $pK^S_{a2} = 9.72$.

The influence of oxalic acidity on mobility may be described in terms of two successive adsorption equilibria, the first one conducive to the neutralization of positive protonic charge, and the second one originating a charge reversal. It is shown that the apparent affinity for this latter mode is lower in one of the samples, suggesting that surface complexation constants may in fact be sensitive to the history of hydrous chromium(III) oxide particles.

The three samples show similar dissolution behaviour but the specific rates differ, in one case by two orders of magnitude. This difference is explained in terms of the influence of crosslinking on the reactivity.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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INTRODUCTION

The surface complexation approach has dealt with considerable success with a variety of phenomena taking place at the interface metal oxide particle / aqueous solution: generation of electrical charges and potentials in mineral acids, adsorption of inorganic and organic ions, dissolution kinetics, structural evidence. In this context, the behaviour of chromium hydrous oxides has, in a sense, been disappointing; for example, even after many years of exploration of systems and concepts, there is not yet a well established set of acidity constants to describe the surface of chromium(III) hydrous oxides.[1–11] The reasons for this failure seem to stem from the peculiar properties of Cr(III): its d^3 electronic configuration, and the unavailability of accessible redox levels, makes substitution reactions extremely slow. This characteristic gives rise to this sluggish interfacial reaction of the materials with water and solutes, and also affects the structural properties of the materials. Crystalline α-Cr_2O_3 of adequate high surface area is difficult to prepare, and hydrous oxides are in fact a group of compounds in which the Cr(III) coordination polyhedra may differ widely, thus giving rise to disparate interfacial behaviours.

In this sense, the work of Matijević has been outstanding, focusing on carefully planned experiments rather than on unwarranted modelling. This group has explored the behaviour of chromium hydrous oxides for many years in a series of papers, which include the description of a technique for preparing monodisperse particles[12] and a demonstration of the profound influence of anions on the interfacial behaviour of the prepared particles.[1,6]

In this paper, we present a study of three different hydrous chromium(III) oxides prepared in sulphate free media; both their electrophoretic mobilities and their rates of dissolution were measured in mineral and oxalic acid media. The results demonstrate that different preparative routes do indeed yield particles with different surface and bulk structures. This effect is observed even when sulphate and chloride are excluded during the synthesis of the particles.

EXPERIMENTAL

Synthesis of $Cr_2O_3 \cdot nH_2O$

A(1) and A(2) oxides

30 cm^3 of 27% ammonia was added to 600 cm^3 of 0.2 mol dm^{-3} Cr(NO$_3$)$_3$ at 90 °C. The mixture was left at this temperature for 1 h; the precipitate was filtered off, washed repeatedly with doubly distilled water and oven dried at 60 °C. The solids were characterized by chemical and thermogravimetric analysis, XRD, SEM and sur-

face area (BET) measurements. Two batches were synthesized, oxide samples A(1) and A(2). Oxide sample A(2) was aged for one year in a vacuum desiccator.

A(3) oxide

A 2×10^{-2} mol dm^{-3} Cr(NO$_3$)$_3$ solution was fast neutralized with NaOH until the molar ratio [OH$^-$]$_0$ / [Cr(III)]$_0$ was 2.5. The suspension of the »active« Cr(OH)$_3$ thus obtained [13] was heated at 80 °C for 48 h; this step leads to polymeric soluble species.[14] The polymeric solution was neutralized until the molar ratio [OH$^-$]$_0$ / [Cr(III)]$_0$ was 3.0, and the resulting suspension was aged at 80 °C for 48 h. The solid was separated on a cellulose nitrate filter of pore size 0.2 μm, repeatedly washed with doubly distilled water and dried in a vacuum oven at 50 °C. The oxide was dialyzed until the conductance of the supernatants was 0.1 mS cm^{-1}.

A concentrated aqueous suspension was prepared for the three oxides, and stored in a polypropylene bottle. Ageing times were from 30 to 140 days at room temperature. Table I shows the characteristics of the chromium oxide samples. The shape (spherical) and the modal size were determined by SEM.

TABLE I

Characteristics of oxides Cr$_2$O$_3 \cdot n$H$_2$O

Sample	Chromium $w \times 100$	$n^{(a)}$ (mol H$_2$O/ mol Cr$_2$O$_3$)	Surface area m^2 g^{-1}	X-ray diffraction	Particle size (diameter) μm
A(1)	15.5 ± 0.1	28	6.1 ± 0.1	Amorphous	0.4 ± 0.1
A(2)	29.7 ± 0.1	11	36.2 ± 0.1	Amorphous	0.4 ± 0.1
A(3)	33.5 ± 0.1	14	240 ± 0.5	Amorphous	0.2 ± 0.1

[a] From thermogravimetric analysis.

Kinetic Measurements

20 mg Cr$_2$O$_3 \cdot n$H$_2$O was poured onto a magnetically stirred solution containing 0.1 mol dm^{-3} oxalic acid at pH = 4.0 in a cell provided with a jacket to circulate water at 65.0 ± 0.1 °C, or, alternatively, an aliquot of an aqueous suspension of the aged oxides was mixed with the oxalic acid solution; the surface/volume ratio was the same in both procedures. Ionic strength was fixed essentially by K(HC$_2$O$_4$) at 0.1 mol dm^{-3}. To follow the dissolution reaction, aliquots were withdrawn periodically and filtered through 0.45 pore size cellulose acetate membranes. Total chromium concentration was measured in the filtrate by atomic absorption spectrometry using a Varian AAR 5 apparatus.

Electrophoretic Measurements

Small amounts of amorphous (fresh or aged) oxides were suspended in 10^{-2} mol dm^{-3} KCl solutions, pH was adjusted and the suspensions were left to equili-

brate for 24 h. Due precautions were taken to avoid contact with atmospheric CO_2. Electrophoretic mobilities in mineral acid or base were measured in the pH range 3.0–11.0 at 25.0 ± 0.1 °C. The measurements at each oxalic acid concentration were carried out adjusting the pH of a suspension of the desired oxalate concentration, pre-equilibrated at pH = 4.0, 25.0 ± 0.1 °C and of ionic strength 0.01 mol dm^{-3} (KCl). After pH adjustment (within the range 3.0–11.0), the suspensions were equilibrated for 24 h and mobilities were measured in a PenKem S3000 equipment.

Mobilities were transformed into ζ-potentials using a modified Ohshima's procedure[15] for spherical symmetry. A PC-program was developed in our laboratories to calculate the ζ-potentials for spherical or cylindrical[16] particles from electrophoretic mobilities data, particle size, ionic strength and temperature, using Ohshima's approach.

RESULTS AND DISCUSSION

Electrophoretic Mobilities

Measurements of mobilities as a function of ageing time (up to 100 days) showed that the profiles in mineral acid shifted, upon ageing towards the acid side, whereas in oxalate media the mobilities were insensitive to ageing. Figures 1–3 show the mobility / pH profiles for the three samples, meas-
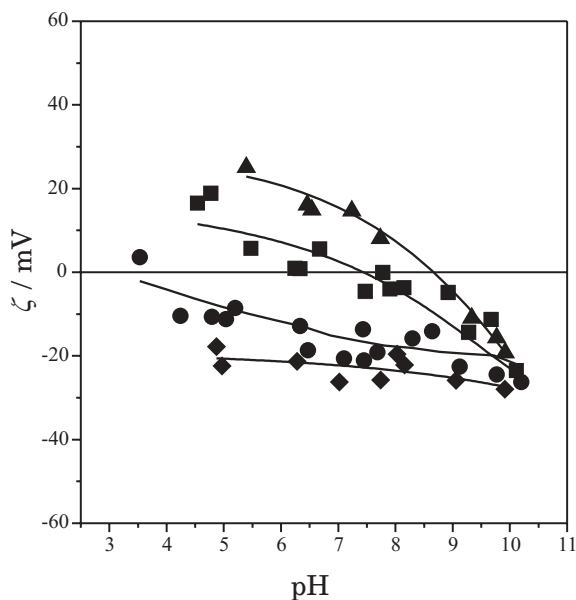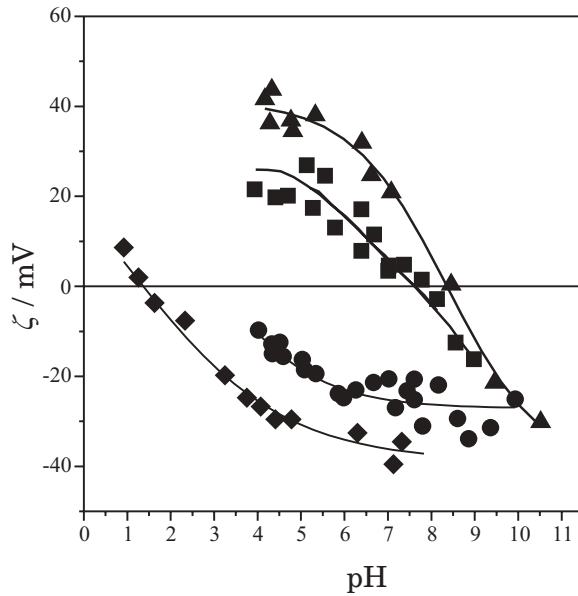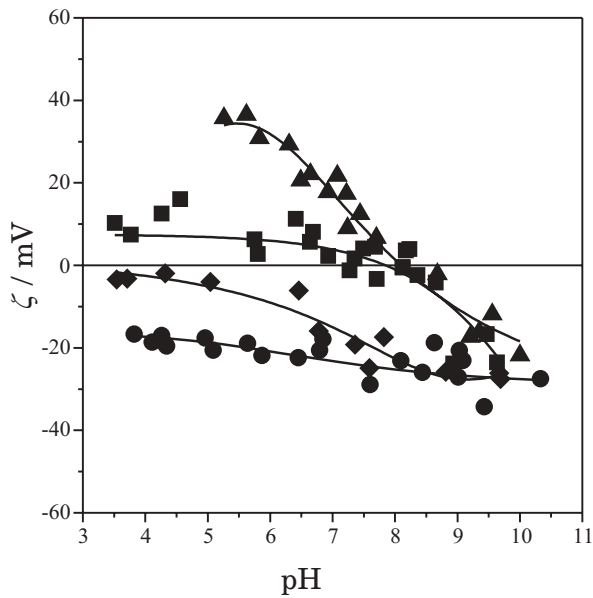

Figure 1. ζ-potentials of A(1) oxide as a function of pH in 10^{-3} mol dm^{-3} KCl, at various oxalic acid concentrations: (▲) 0; (■) 5×10^{-5}; (●) 5×10^{-4} and (◆) 5×10^{-3} mol dm^{-3}.

Figure 2. ζ-potentials of A(2) oxide as a function of pH in 10^{-3} mol dm^{-3} KCl, at various oxalic acid concentrations: ($\blacktriangle$) 0; ($\blacksquare$) 5×10^{-5}; ($\bullet$) 5×10^{-4} and ($\blacklozenge$) 5×10^{-3} mol dm^{-3}.

Figure 3. ζ-potentials of A(3) oxide as a function of pH in 10^{-3} mol dm^{-3} KCl, at various oxalic acid concentrations: ($\blacktriangle$) 0; ($\blacksquare$) 5×10^{-5}; ($\blacklozenge$) 5×10^{-4} and ($\bullet$) 5×10^{-3} mol dm^{-3}.

ured at various oxalate concentrations. Aged samples in mineral acid, once the electrokinetic equilibrium was reached, yielded isoelectric points consistent with the values reported in the literature.[7–9,13]

The isoelectric points of the oxides in mineral media were 8.6, 8.5 and 8.3, respectively, for samples A(1), A(2) and A(3). Thus, the intrinsic acidities of the surfaces do not differ much; this result is to be contrasted with the wide variety of results reported in the literature.[1,6] We have found in the literature only one set of acidity constants for »hydrous chromium oxide«, which was derived using the triple layer model, and optimized for a measured isoelectric point of 9.2.[17] These values, $pK^S_{a1} = 6.9$ and $pK^S_{a2} = 11.5$, reflect the high isoelectric point used for the calculations. The wealth of the information points to lower values of the isoelectric point, as illustrated by the work of Sprycha and Matijević,[8] and in line with those found earlier by us.[13]

We have postulated before that the points of zero charge of hydrous metal oxides should be shifted from the solution values simply because of the differing contribution of solvation energy to the adsorption of anionic and cationic species.[13,18] The differences between the obtained values for hydrous chromium oxides particles and the corresponding solution values are in the range (–0.2) – (–0.5). Small shifts are expected on the basis of the most simple case of the solvation energy model, when the hydration energy of dissolved cations $M(OH)_2^+$ is more negative than the hydration energy of surface cations $\equiv M–OH^+$. Thus, for hydrous chromium oxides at least, the isoelectric point may be interpreted following this line.

In a more general case, the small shifts may be positive or negative, depending on the solvatation characteristics of surface cations and anions; for α-Fe_2O_3, the shift is indeed +0.5.[13]

If the changes in surface acidity, as compared to solution acidity, are due to solvation factors, the pK^S_{a1} and pK^S_{a2} values corresponding to equilibria (1) and (2) should also be related to the solution values, with larger shifts in the former.

$$\equiv MOH_2^+ \; \rightleftharpoons \; \equiv MOH + H^+ \qquad\qquad (1)$$

$$\equiv MOH \; \rightleftharpoons \; \equiv MO^- + H^+ \qquad\qquad (2)$$
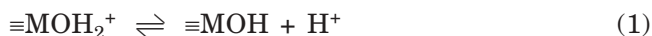
This simple model suggests that, for a series of hydrous oxides, ΔpK^S_a values, where $\Delta pK^S_a = pK^S_{a2} - pK^S_{a1}$, should correlate with the corresponding $\Delta pK_{a(aq)}$ values, where $\Delta pK_{a(aq)} = pK_{a2(aq)} - pK_{a1(aq)}$. The corresponding solution equilibria are given in Eqs. (3) and (4)

$$M(OH)_2{}^+ + H_2O \rightleftharpoons M(OH)_3 + H^+ \tag{3}$$

$$M(OH)_3 + H_2O \rightleftharpoons M(OH)_4{}^- + H^+ \tag{4}$$
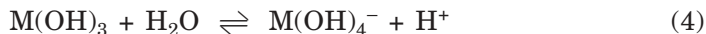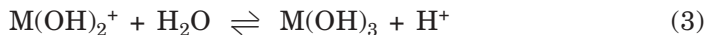
For iron and chromium oxides, the relationship

$$\Delta(\mathrm{p}K_a) = \Delta \mathrm{p}K^S{}_a - \Delta \mathrm{p}K_{a(aq)} = \text{constant} \tag{5}$$

with $\Delta \mathrm{p}K^S{}_a(\mathrm{Fe}) = 5.15$ (Ref. 19), $\Delta \mathrm{p}K_{a(aq)}(\mathrm{Fe}) = 3.1$ (Ref. 20), and $\Delta \mathrm{p}K_{a(aq)}(\mathrm{Cr})$ = 0.5 (Ref. 20) leads to $\Delta \mathrm{p}K^S{}_a(\mathrm{Cr}) = 2.55$. Assuming that the isoelectric point measured in mineral media is identical with the point of zero charge (pH_0 = p.z.c. = $0.5\,[\mathrm{p}K^S{}_{a1} + \mathrm{p}K^S{}_{a2}] = 8.45$), the values $\mathrm{p}K^S{}_{a1} = 7.17$ and $\mathrm{p}K^S{}_{a2} = 9.72$ can be estimated for hydrous chromium oxides.

Comparison of these values with those reported by Crawford et al.[17] shows that not only $\{0.5\,[\mathrm{p}K^S{}_{a1} + \mathrm{p}K^S{}_{a2}]\}$ is lower in our case; also, $\Delta \mathrm{p}K^S{}_a$ is appreciably lower. The low $\Delta \mathrm{p}K^S{}_a$ is in line with the solution behaviour, and describes an intrinsic feature of the Cr(III) acidity.

Oxalate brings about a charge reversal in a wide pH range; only at the lowest oxalate concentration in the case of oxide A(3) the shift of the isoelectric point is very small; the main observed effect in this case is a decrease in the positive mobilities in the acidic pH range. To explain the curves of Figures 1–3, it suffices to assume two modes of adsorption. These modes may be described in a variety of ways, but their essential characteristics should be as follow:

(a) The first mode should imply an electroneutral adsorption in the pH range close to the isoelectric point in mineral acid, and neutralization of positive charge in more acidic media. For example,
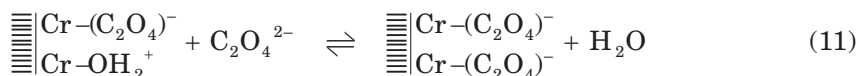
$$\equiv\!\mathrm{Cr}\!-\!\mathrm{OH} + C_2O_4{}^{2-} + 2\,H^+ \rightleftharpoons\; \equiv\!\mathrm{Cr}\!-\!(C_2O_4H) + H_2O \tag{6}$$

$$\equiv\!\mathrm{Cr}\!-\!\mathrm{OH}_2{}^+ + C_2O_4{}^{2-} + H^+ \rightleftharpoons\; \equiv\!\mathrm{Cr}\!-\!(C_2O_4H) + H_2O \tag{7}$$
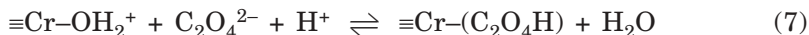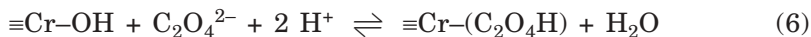
(b) The second mode should account for the reversal of surface charge. For example,

$$\equiv\!\mathrm{Cr}\!-\!\mathrm{OH} + C_2O_4{}^{2-} + H^+ \rightleftharpoons\; \equiv\!\mathrm{Cr}\!-\!(C_2O_4)^- + H_2O \tag{8}$$

$$\equiv\!\mathrm{Cr}\!-\!\mathrm{OH}_2{}^+ + C_2O_4{}^{2-} \rightleftharpoons\; \equiv\!\mathrm{Cr}\!-\!(C_2O_4)^- + H_2O \tag{9}$$
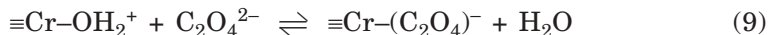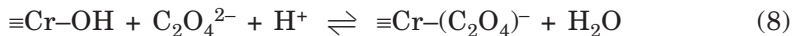
(c) The first mode should be important at low oxalate concentrations, and the second one is more important in the more concentrated oxalate media, to account for the shape of the curves in Figure 3 (sample A(3)).

(d) The surface species should not be related by simple protolytic equilibrium, as the notation employed in Eqs. (6–9) may suggest; rather, successive steps, sensitive to the surface topography are required to explain the sensitivity of the oxalate dependence on the nature of the sample (see (c) above). Possible structures for the surface complexes, composed of two vicinal chromium centres, are those indicated in the successive equilibria (10) and (11).

$$\begin{Vmatrix} Cr-OH \\ Cr-OH_2^+ \end{Vmatrix} + C_2O_4{}^{2-} + H^+ \rightleftharpoons \begin{Vmatrix} Cr-(C_2O_4)^- \\ Cr-OH_2^+ \end{Vmatrix} + H_2O \qquad (10)$$

$$\begin{Vmatrix} Cr-(C_2O_4)^- \\ Cr-OH_2^+ \end{Vmatrix} + C_2O_4{}^{2-} \rightleftharpoons \begin{Vmatrix} Cr-(C_2O_4)^- \\ Cr-(C_2O_4)^- \end{Vmatrix} + H_2O \qquad (11)$$
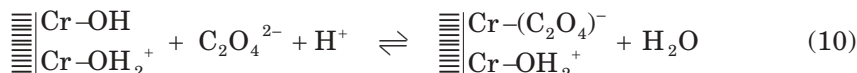
Oxide A(3) differs from oxides A(1) and A(2) in the decreased availability of the protonated vicinal site to that on which the first oxalate was adsorbed; the main reaction at low oxalate concentration is (10), conducive to a decrease of positive charge, but without the charge reversal brought about by (11). Further adsorption of oxalate, as shown in Eq. (11) is thus not important in oxide A(3) at the lowest oxalate concentrations. Different affinity of the various surfaces for the mode depicted in Eq. (11) sets the limits of applicability of the simplest versions of the surface complexation approach: stability constants may be sensitive to the history of the solid.

Dissolution Kinetics

Rate data were interpreted using the modified contracting volume rate law:

$$1 - (1-f)^{1/3} = \frac{k_A w_0 S_0{}^s (t-t_0)}{3} \qquad (12)$$

$S_0{}^s$ is the specific surface area, f is the fractional extent of dissolution, $f = (w_0 - w)/w_0$, where w_0 and w are the initial and instantaneous mass of residual solid, k_A is the specific rate constant (rate per unit area / m^{-2} s^{-1}) and t_0 is an empirical induction time.

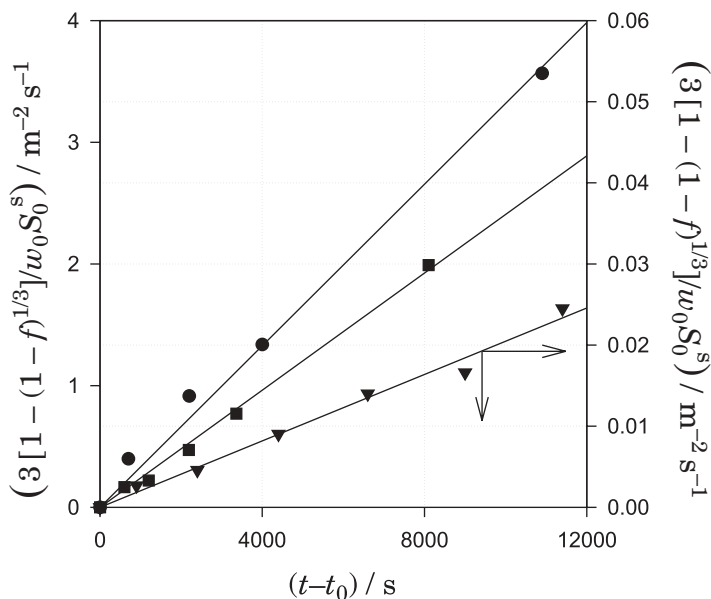Figure 4. Linear profiles calculated according to Eq. (12) for oxides samples: (●), A(1); (■), A(2) and (▼), A(3), $[H_2C_2O_4]$ = 0.1 mol dm^{-3}, pH = 4.0, 65 °C.

A good linear fitting was obtained for the time dependence of $3[1 - (1 - f)^{1/3}]/$ $/w_0 S_0^s$, as shown in Figure 4, for the three oxide samples studied. The linearity of the plots, or the constancy of k_A, implies that after the induction period $(t \geq t_0)$, the surface reaches a steady state condition, in which the rate per unit area is constant.

Reactivity behaviours of the different samples used in this study are qualitatively similar, but their intrinsic reactivities are different. The reactivity trend is A(1) > A(2) >> A(3); the k_A values are, respectively, 3.18×10^{-4}, 2.47×10^{-4} and 2.03×10^{-6} m^{-2} s^{-1}. The dissolution behaviour of the oxide samples aged in aqueous solution for between 30 and 140 days is indistinguishable from that of fresh materials.

The electrokinetic results and the dissolution kinetics demonstrate a close similarity between the surfaces of samples A(1) and A(2), and an appreciably different case for A(3). In an earlier paper,[21] we discussed the small differences between the reactivity of samples A(1) and A(2); now we see that their electrokinetic behaviour is also similar. For the proposed preparative procedure, it is thus concluded that reproducible surface properties result; a steady state composition is reached, however, only after an adequate ageing period, of the order of 60 days in water, much shorter than in the presence of oxalic acid media (less than one day).

The structure of oxide A(3) is appreciably different. Highly crosslinked polymers are formed during the solution stage, and they later unite to form the solid (see Experimental section and Refs. 14, 22–24). Our results demonstrate that this structure is more resistant to acid attack, in line with our previous contention that cross-linking and the degree of oxolation determine the reactivity toward acid dissolution.[25]

CONCLUSIONS

The acidity of hydrous chromium oxides can be described by the one site-two constants surface complexation model, with a low ΔpK^S_a value reflecting the chemical properties of Cr(III).

An electroneutral mode accounts for the noticeable decrease in ζ-potentials brought about by oxalate adsorption. At higher oxalate concentrations a second adsorption mode produces charge reversal. The relative importance of both adsorption modes is sensitive to the structure of the sample, suggesting that surface complexation »constants« may depend on the sample history.

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SAŽETAK

Elektrokinetičko ponašanje i interakcija različitih oksida kroma(III) s oksalnom kiselinom

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Tri uzorka kromovih(III) oksida pripravljeni su različitim postupcima i mjerene su njihove elektrokinetičke pokretljivosti. U vodenom mediju njihove izoelektrične točke izmjerene su pri pH = 8,45 ± 0,15. Doprinos solvatacijske energije ukupnoj energiji ionske adsorpcije pomaknuo je tu vrijednost za –0,35 ± 0,15. Na osnovi predloženog modela određene su konstante površinske kiselosti kromova(III) oksida: pK^S_{a1} = 7,17 i pK^S_{a2} = 9,72.

Utjecaj oksalne kiseline na elektroforetsku pokretljivost može se opisati dvjema uzastopnim adsorpcijskim ravnotežama: prva vodi do neutralizacije pozitivnog naboja protona, a druga leži u promjeni naboja. Za jedan uzorak je utvrđeno da konstante površinskog kompleksiranja ovise o načinu priprave čestica kromova III oksida.

Tri uzorka kromova(III) oksida pokazala su slično otapanje, ali u jednom slučaju specifična brzina otapanja razlikovala se za dva reda veličine zbog utjecaja umrežavanja na reaktivnost.