Introduction

Several publications deal with the charging of mixed oxide suspensions [1-7]. It has been shown that components are charged independently and so the overall charge is the sum of the charges of the components [6]. Also, the overall point of zero charge (PZC) was found between the values characterizing the components but was dependent on their fractions in the mixture. The aim of this article is to examine the applicability of the “mass-titration” method [8-10] to mixed-oxide dispersions.

Theoretical

According to the assumption of independent charging the overall (total) charge \(Q\) of colloidal particles is the sum of all contributions. For the mixture of silica (s) and hematite (h) examined

\[
Q = Q_s + Q_h
\]

The overall surface charge density \(\sigma\) is related to the fraction of the surface areas \(f\) of each component by

\[
\sigma = f_s \sigma_s + f_h \sigma_h = f_s \sigma_s + (1 - f_s) \sigma_h
\]

where \(f\) is proportional to the mass fraction \(w\) and specific surface area \(s\) of a component

\[
f_h = \frac{s_h w_h}{s_h w_h + s_s w_s}
\]

In an aqueous dispersion of a metal oxide, protonation (p) and deprotonation (d) of amphoteric surface -OH groups take place [11]. In the mixture of hematite and silica particles, the following reactions are responsible for surface charging

\[
\equiv \text{FeOH} + H^+ \rightarrow \equiv \text{FeOH}_2^+; \Delta\varepsilon_{p,h}
\]

\[
\equiv \text{FeOH} \rightarrow \equiv \text{FeO}^- + H^+; \Delta\varepsilon_{d,h}
\]

\[
\equiv \text{SiOH} + H^+ \rightarrow \equiv \text{SiOH}_2^+; \Delta\varepsilon_{p,s}
\]

\[
\equiv \text{SiOH} \rightarrow \equiv \text{SiO}^- + H^+; \Delta\varepsilon_{d,s}
\]

Abstract Surface charge and point of zero charge (PZC) in an aqueous silica-hematite mixed system were determined as a function of pH and of mixture composition by “mass titration” and acid-base titration of the suspension. The experiments showed that charging was independent, i.e. the overall surface charge was approximately equal to the sum of the surface charges of each oxide. The PZC of metal oxide mixtures corresponds to the pH where the net (overall) surface charge is zero, while one oxide bears a positive and the other a negative charge. The PZC of mixed oxides was found to lie between the PZC of pure oxides, depending on specific surface area, mass fraction and the PZC of each oxide in the mixture. It is shown that “mass titration” could be used as a method for determination of the PZC and surface charge of pure oxides and that it also may be applied to their mixtures.

Key words Mixed oxides – Point of zero charge – Surface charge – Mass titration
The extent ($\bar{\zeta}$) of each reaction depends on pH and the corresponding equilibrium constant. In addition to surface reactions, the water dissociation equilibrium influences consumption of $H^+$ or $OH^-$ ions in the bulk of the solution:

$$OH^- + H^+ \rightarrow H_2O; \Delta \bar{\zeta}_n$$

(8)

Accordingly, the change in the number of $H^+$ ions in the bulk of the solution is given by

$$\Delta n(H^+) = -\Delta \bar{\zeta}_{p,h} + \Delta \bar{\zeta}_{d,h} - \Delta \bar{\zeta}_{p,s} + \Delta \bar{\zeta}_{d,s} - \Delta \bar{\zeta}_n$$

(9)

while the change in the number of $OH^-$ ions depends on the extent of neutralization only

$$\Delta n(OH^-) = -\Delta \bar{\zeta}_n$$

(10)

From Eqs. (9) and (10) one obtains

$$\Delta n(H^+) - \Delta n(OH^-) = -\Delta \bar{\zeta}_{p1} + \Delta \bar{\zeta}_{d1} - \Delta \bar{\zeta}_{p2} + \Delta \bar{\zeta}_{d2}$$

(11)

Surface concentrations ($I$) of surface sites are related to the extents of the relevant reactions, and so the difference in changes in $H^+$ and $OH^-$ bulk concentrations is equal to

$$\Delta c(H^+) - \Delta c(OH^-) = -\frac{A_h}{V} \left[ I'(FeOH^+_2) - I'(FeO^-) + A_s [I'(SiOH^+_2) - I'(SiO^-)] \right]$$

(12)

When the mass-titration method [8–10] is applied for determining the charge of a mixed-oxide system, portions of mixed solid powder are added to water or to an aqueous electrolyte solution. The initial pH$_0$ changes to the new equilibrium value, pH$_y$, which depends on the mass concentration of solid ($y$). Changes in $H^+$ and $OH^-$ ion concentrations can be obtained from pH measurements by

$$\Delta c(H^+) = \frac{c^o}{y} \left( 10^{-pH_y} - 10^{-pH_h} \right)$$

(13)

$$\Delta c(OH^-) = \frac{c^o}{y} \left( 10^{pH_y-pK_w} - 10^{pH_0-pK_w} \right)$$

(14)

where $y$ is the activity coefficient of monovalent ions given by the Debye-Hückel equation, $c^o$ is the standard value of concentration ($c^o = 1$ mol dm$^{-3}$) and $pK_w$ is the negative logarithm of the equilibrium constant of water dissociation.

The overall surface charge in the inner part of the Helmholtz layer, in the absence of countermion association and specific adsorption, is defined as

$$\sigma_0 = F[I'(FeOH^+_2) - I'(FeO^-) + I'(SiOH^+_2) - I'(SiO^-)]$$

(15)

where $F$ is the Faraday constant. Equations (2) and (15) yield

$$\Delta c(H^+) - \Delta c(OH^-) = -\frac{A}{VF} \sigma_0$$

(16)

where $A$ is the total surface area of the solid phase (sum of surface areas of both oxides), and $V$ is the solution volume. According to Eqs. (14)–(16), the overall surface charge density can be simply obtained from pH dependency on the mass concentration by

$$\sigma_0 = -\frac{VF}{A} \left[ 10^{-pH_y} - 10^{-pH_h} - 10^{pH_0-pK_w} + 10^{pH_0-pK_w} \right]$$

(17)

The above relationship suggests that $\sigma_0$ approaches zero as the mass concentration of solid powder (total surface area) increases. Therefore, as in the case of a one-component system, the PZC condition may be achieved by preparing a highly concentrated dispersion. For a two-component system, the (overall) PZC means that the total charge of all particles is zero, but particles of each component bear opposite charges.

### Experimental

**Chemicals**

All chemicals (HNO$_3$, KOH, KNO$_3$; Merck, Germany) used in the experiments were of analytical purity grade. The hematite (Alfa, Johnson Matthey, Karlsruhe, Germany) and silica (Aerosil 200, Degussa, Germany) were purified by extensive washing. The specific surface area of silica was 200 m$^2$ g$^{-1}$ and that of hematite 8.8 m$^2$ g$^{-1}$, as determined by the Brunauer-Emmett-Teller method.

Experiments were performed in the pH region (4 < pH < 7) in which no dissolution of hematite and silica take place.

**Mass titration**

The initial pH (pH$_0$ = 5) was adjusted with addition of HNO$_3$. The constant ionic strength of $5 \times 10^{-3}$ mol dm$^{-3}$ was controlled by KNO$_3$. First, a paste of pure silica, hematite and of different silica-hematite mixtures was prepared. The paste contained a small amount of initial aqueous solution, which enabled simple additions and redispersion of particles. In the course of mass titration, weighted portions of paste were added to the thermostated aqueous solution (dispersion). After each addition, the system was exposed to ultrasound (ultrasonic probe) for 10 min and equilibrated under stirring for the next 30 min. The pH was measured using a combined glass-Ag/AgCl electrode (Methrom). The systems were kept under an argon atmosphere and thermostated (25.0°C).

**Acid base titration**

The basic (KOH) suspension ($y = 10$ g dm$^{-3}$) was titrated with acid (HNO$_3$). The ionic strength was adjusted with KNO$_3$. Prior to titration, the system was sonicated for 10 min. During the experiment the system was thermostated (25.0°C), stirred and kept under an argon atmosphere. After each additional of acid, the pH was measured using a combined glass-Ag/AgCl electrode (Methrom). The systems were kept under an argon atmosphere and thermostated (25.0°C). Automatic titration was performed using a Titrino-Methrom system. Surface charge densities were obtained by the normal procedure [12], by comparison with a blank titration. The PZC was obtained from the cross section of charge density functions.