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Application of »Mass Titration« to Determination of Surface Charge of Metal Oxides

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The mass titration method, used for the point of zero charge determination, was extended to the measurement of the surface charge density. The results agree with the common method, which is the acid-base titration of the colloidal suspension. The advantage of mass titration is that one does not need to perform blank titration, instead one simply adds metal oxide powder to the electrolyte aqueous solution of known pH. To cover the pH range above and below the point of zero charge, two experimental runs are necessary.

INTRODUCTION

The »Mass titration method« was found to be a suitable tool in determination of the point of zero charge (p.z.c) of metal oxides. It was originally developed for pure metal oxides[1] and later extended so that it can be used also for contaminated samples.[2] The principle of the method is simple; one needs to add subsequent portions of metal oxide powder to the water or an aqueous electrolyte solution, which might be acidified or may contain a base. The pH of the system changes gradually and approaches a constant value, which is the point of zero charge in the case of pure oxide. If the sample is contaminated, *i.e.* if it contains a certain portion of acid or base, the final pH is higher or lower than p.z.c, depending on the type and amount of the acid or base in the powder. In the case of contamination, one needs to perform an »acid-base« titration of the concentrated suspension and the inflexion point

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

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provides the information on the p.z.c., and also on the fraction of impurities in the powder. The method is simple from the experimental point of view and has also some other advantages since the experiment can be performed at an extremely low ionic strength, which cannot be achieved in the case of »acid-base« type of titration. This is important because only at low ionic strengths the point of zero charge coincides with the isoelectric point. The advantage of the »Mass titration method« was demonstrated when the temperature dependency of the point of zero charge was examined.[3–5] It was sufficient to determine the mass concentration of the solid producing the pH equal to the point of zero charge and to measure the pH of such concentrated system as a function of temperature.

The aim of this work is to extend the use of the »Mass titration method« to determination of the surface charge, but not only to the p.z.c. determination, as it was applied before. Two advantages over the classical »acid-base« potentiometric titration[6–11] may be expected: comparison with blank titration in the absence of solid is avoided and no experiments at different ionic strengths are necessary for the location of p.z.c. either.

THEORETICAL

Surface charge of an oxide in aqueous environment is the result of the protonation (p) and deprotonation (d) of amphoteric surface sites, which will be denoted by MOH, where M stands for a metal. The corresponding surface reactions may be written as follows

$$\mathrm{MOH} + \mathrm{H}^+ \rightarrow \mathrm{MOH_2}^+; \quad \Delta\xi_\mathrm{p} \tag{1}$$

$$\mathrm{MOH} \rightarrow \mathrm{MO}^- + \mathrm{H}^+; \quad \Delta\xi_\mathrm{d} \tag{2}$$

Symbol ξ denotes the extent of the corresponding reactions, *i.e.* the »number of moles« of the reactions (1–3). In addition to the above reactions, the association of counterions with surface charge groups $\mathrm{MOH_2}^+$ and MO^- may take place. Surface reactions are usually accompanied by neutralization in the bulk of the solution

$$\mathrm{OH}^- + \mathrm{H}^+ \rightarrow \mathrm{H_2O}; \quad \Delta\xi_\mathrm{n} \tag{3}$$

In an aqueous metal oxide suspension, a change in the equilibrium state may be initiated, for example, by addition of an acid or a base. The following consideration takes into account the addition of the solid phase (powder) to the aqueous solution or suspension. The solid phase may contain a certain portion of acid or base as impurities, so these contributions should be also taken into account when considering the change in the amounts (moles) of free hydronium ions, $\Delta n(\mathrm{H}^+)$, and free hydroxyl ions, $\Delta n(\mathrm{OH}^-)$, in the bulk of the solution. Acidic impurities will be represented by nitric acid, while the potassium hydroxide will represent basic impurities. Accordingly,

$$\Delta n(\mathrm{H}^+) = \Delta n(\mathrm{HNO_3}) - \Delta\xi_\mathrm{p} + \Delta\xi_\mathrm{d} - \Delta\xi_\mathrm{n} \tag{4}$$

$$\Delta n(\mathrm{OH}^-) = \Delta n(\mathrm{KOH}) - \Delta\xi_\mathrm{n} \tag{5}$$

According to Eqs. (4) and (5),

$$\Delta n(\mathrm{H}^+) - \Delta n(\mathrm{OH}^-) = \Delta n(\mathrm{HNO_3}) - \Delta n(\mathrm{KOH}) - \Delta\xi_\mathrm{p} + \Delta\xi_\mathrm{d} \tag{6}$$

In the following derivation, the solution in the absence of solid oxide will be considered as the initial state, while the final state will be the equilibrated suspension after addition of the solid. Therefore, the mass concentration is zero in the initial and γ in the final state. The portions of acidic or basic impurities (if any are present) are expressed as fractions (k or b) equal to the amount (moles) of acid or base *per* mass of solid. Accordingly, the amount of acid or base added to the system is proportional to the mass of solid

$$\Delta n(\mathrm{HNO_3}) = mk \tag{7}$$

$$\Delta n(\mathrm{KOH}) = mb \tag{8}$$

The initial state is defined in such a way that the change of the extent of protonation (reaction 1) is equal to the amount of created positive groups

$$\Delta\xi_\mathrm{p} = sm\Gamma(\mathrm{MOH_2}^+) \tag{9}$$

where Γ denotes surface concentration, and m the mass of solid of a specific surface area s. Analogously, the extent of deprotonation (reaction 2) is equal to

$$\Delta\xi_\mathrm{d} = sm\Gamma(\mathrm{MO}^-) \tag{10}$$

Equations (6–10) yield the relationship between the change in H^+ and OH^- concentrations in the bulk of the solution and the mass concentration of the suspension

$$\Delta c(\mathrm{H}^+) - \Delta c(\mathrm{OH}^-) = \gamma\,(k\text{–}b) - \gamma\, s[\Gamma(\mathrm{MOH_2}^+) - \Gamma(\mathrm{MO}^-)] \tag{11}$$

where γ is the mass concentration of the solid phase. The surface charge in the inner part of the Helmholtz layer, in the absence of counter ion association and specific adsorption, is defined as

$$\sigma_0 = F[\Gamma(\mathrm{MOH_2}^+) - \Gamma(\mathrm{MO}^-)] \tag{12}$$

where F is the Faraday constant. Equations (11) and (12) yield

$$\Delta c(\mathrm{H}^+) - \Delta c(\mathrm{OH}^-) = \gamma\,[(k-b) - \frac{s}{F}\sigma_0] \tag{13}$$

Changes in the concentrations of H^+ and OH^- ions may be obtained from pH measurements

$$\Delta c(\mathrm{H}^+) = \frac{c^\circ}{y}(10^{-\mathrm{pH}_\gamma} - 10^{-\mathrm{pH}_0}) \tag{14}$$

$$\Delta c(\mathrm{OH}^-) = \frac{c^\circ}{y}(10^{\mathrm{pH}_\gamma - \mathrm{p}K_\mathrm{w}} - 10^{\mathrm{pH}_0 - \mathrm{p}K_\mathrm{w}}) \tag{15}$$

where y is the activity coefficient given by the Debye-Hückel equation, c° is the standard value of concentration ($c^\circ = 1$ mol dm^{-3}) and $\mathrm{p}K_\mathrm{w}$ is the negative logarithm of the equilibrium constant of water dissociation. According to Eqs. (13–15), the surface charge is

$$\sigma_0 = \frac{F(k-b)}{s} - \frac{F}{\gamma s}\frac{c^\circ}{y}\,[10^{-\mathrm{pH}_\gamma} - 10^{-\mathrm{pH}_0} - 10^{\mathrm{pH}_\gamma - \mathrm{p}K_\mathrm{w}} + 10^{\mathrm{pH}_0 - \mathrm{p}K_\mathrm{w}}] \tag{16}$$

In order to evaluate the surface charge by this method, one should know the values of the degree of contamination $k - b$, which may be obtained from the acid – base titration of the concentrated suspension, as shown before.[2] An other approach might involve purification of the sample, which is not always an accurate method. In any case, one may obtain the relative value of the surface charge and locate the zero on the basis of the known point of zero charge

$$\sigma_{0,\mathrm{rell}} = \sigma_0 - \frac{F(k-b)}{s} = -\frac{F}{\gamma s}\frac{c^\circ}{y}\,[10^{-\mathrm{pH}_\gamma} - 10^{-\mathrm{pH}_0} - 10^{\mathrm{pH}_\gamma - \mathrm{p}K_\mathrm{w}} + 10^{\mathrm{pH}_0 - \mathrm{p}K_\mathrm{w}}] \tag{17}$$

The above treatment shows the possibility of determining surface charge by mass titration, *i.e.* by measurement of pH in the system to which solid powder is added in subsequent portions. In order to cover a pH range of interest, at least two experiments should be performed; one with a low and the other with high initial pH. Addition of a large amount of powder will result in pH close to the point of zero charge so that the whole pH range will be covered. In order to measure accurately the surface charge in the vicinity of the point of zero charge, the initial pH should not deviate much from $\mathrm{pH_{pzc}}$.

EXPERIMENTAL

All chemicals (KOH, HNO_3, KNO_3) used in this study were of analytical purity grade. Hematite powder was a commercial sample (Alfa, Johnson Matthey GmbH, Karlsruhe, Germany), of specific surface area of 8.8 m^2 g^{-1}, purified by extensive washing.

Initial pH was adjusted by addition of HNO_3 or KOH. The constant ionic strength of 0.001 mol dm^{-3} was controlled by KNO_3. The weighted amounts of hematite powder were added to the aqueous solution in subsequent portions. The aqueous solution was initially acidic or basic. After each addition and equilibration (15 minutes), the pH was measured by the combined (glass-Ag/AgCl) electrode, Methrom. In order to prevent sedimentation, stirring was applied also during the measurement. The experiments were performed at 25 °C under an argon atmosphere.

The isoelectric point of hematite was measured at the same ionic strength by the Otsuka ELS-800 electrophoretic light scattering.

RESULTS AND DISCUSSION

Figure 1 presents the data of several experimental runs differing in the initial pH, *i.e.* in the acidity of the water to which the solid powder was added. As expected, the increase in mass concentration of hematite causes a change in pH so that the value asymptotically approaches the point of zero charge. The surface charge σ_0 was calculated by means of Eq. (16), assuming that samples did not contain any impurities. The results of the interpretation are presented on Figure 2. Since the isoelectric point measured electrokinetically ($\mathrm{pH_{iep}} = 6.2$) coincides with the point of zero charge, one may conclude that the sample was not contaminated, so interpretation resulted in absolute values of surface charge densities.[12] The reproducibility of the experimental data reflects all problems related to the equilibration of the surface reactions and to pH measurements in the suspension. The results are in good agreement with those obtained by the classical acid-base titration of the suspension, when normalized to the point of zero charge.[6–12]

The accuracy of the results obtained by the acid-base type of titration is related to the consistency with the data of blank titration, *i.e.* to the titration in the absence of the solid phase, while the accuracy of the mass titration method depends on the pH value in the absence of solid powder. Figure 3 demonstrates the effect of the initial pH value on the calculated values of the surface charge for two sets of experimental data, showing the importance

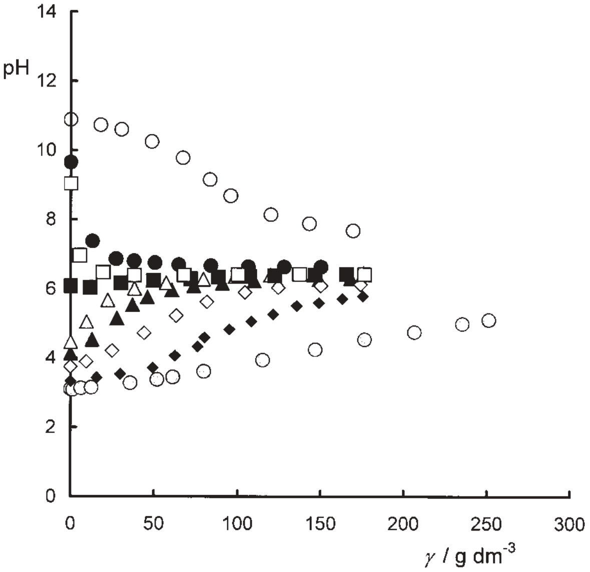

Figure 1. Mass titration of several experimental runs differing in the initial pH of the water to which hematite powder was added. Initial pH: 3.1 (●); 3.3 (◆); 3.7 (◊); 4.1 (▲); 4.5 (Δ); 6.1 (■); 9.0 (□); 9.6 (●); 10.9 (○); Temperature 25.0 °C. Ionic strength: I = 0.001 mol dm^{-3}.

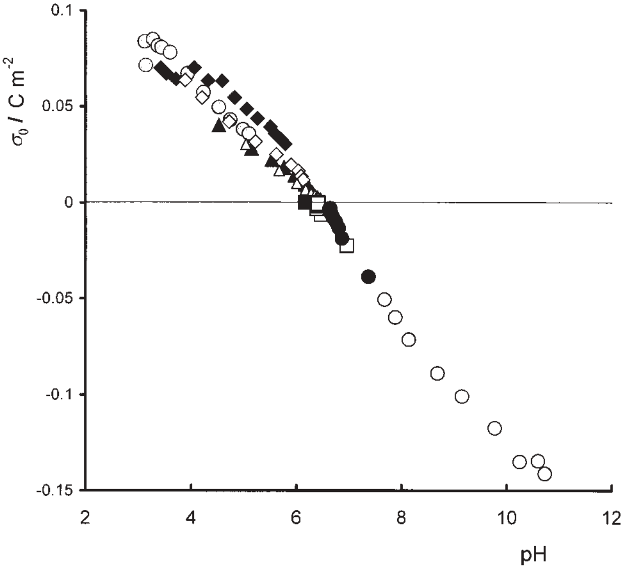

Figure 2. Surface charge density of hematite particles calculated by equation (16) from data presented in Figure 1, using the same symbols. The value of $K_w = 10^{-14}$ was used in calculations.

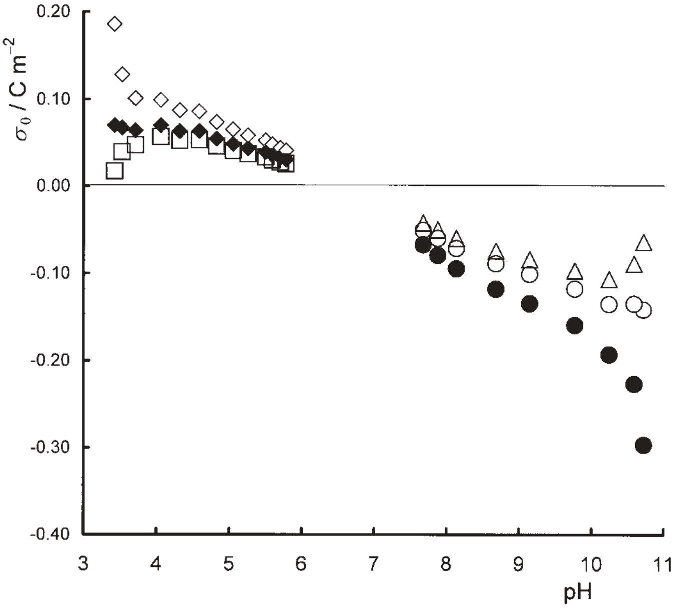

Figure 3. Effect of the initial pH value on the calculated values of the surface charge for two sets of experimental data taken from Figure 1. Acidic region: pH (initial) = 3.4 (◊); 3.33* (◆); 3.2 (□). Basic region: 10.8 (Δ); 10.9* (O); 11.0 (●). The measured initial pH values are denoted by asterisk.

of careful calibration of electrodes. The advantage of mass titration over acid-base titration may lie in the fact that only one calibration of the electrode system is necessary in the first case, while for the acid-base titration method two independent experimental runs are performed, one in the presence and the other in the absence of the solid phase. Another problem is the choice of the value of the equilibrium constant of the water dissociation constant K_w, which is related to the discrepancy between the practical pH-scale, based on the standard buffers, and the theoretical pH scale based on the relative activities of H^+ and OH^- ions.[13] This problem cannot be avoided when pH measurements with glass and reference electrodes are applied, which holds for both acid-base and mass titration methods. The problem could be solved by using the apparent value of the water dissociation constant obtained by the same electrode system using, for example, the Gran method, or in the case of the acid-base titration by the experimental blank titration instead of the theoretical one, based on a certain K_w value.

Figure 4 displays the effect of the chosen value of K_w on the calculated values of the surface charge density.

As expected from equation (16), the effect is pronounced in the basic region where

$$10^{-\mathrm{pH}_\gamma} << 10^{\mathrm{pH}_\gamma - \mathrm{p}K_\mathrm{w}} \tag{18}$$

To conclude, one may consider the mass titration as a complementary method to the common acid-base titration, suitable for surface charge evaluation, which may have advantages in some specific cases.

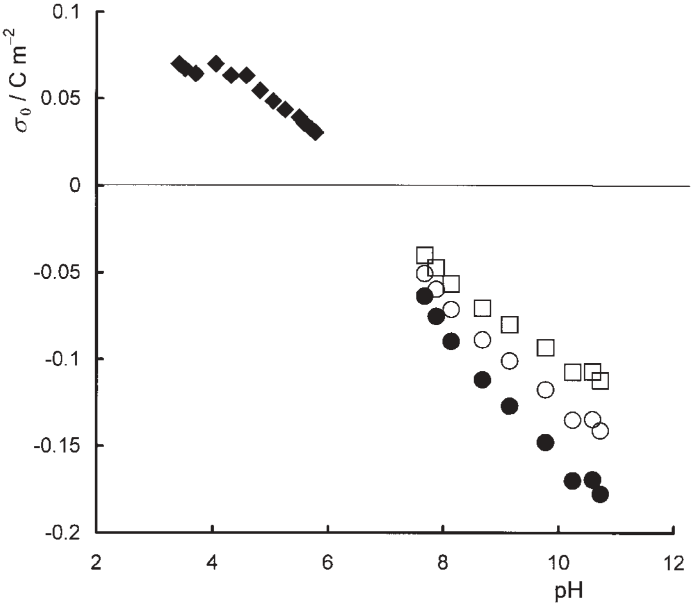

Figure 4. Effect of the chosen value of the equilibrium constant of the water dissociation constant K_w on the calculated values of the surface charge density for experiments presented in Figure 3. The following values were used: pK_w = 13.9 (□); 14.0 (○); 14.1 (●). In the acidic range (◆), no difference was obtained for any assumed value of K_w. In the calculations, the measured initial pH values were used.

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SAŽETAK

Primjena »masene titracije« na određivanje površinskog naboja kovinskih oksida

Tajana Preočanin i Nikola Kallay

Masena titracija, kao metoda za određivanje točke nul naboja, modificirana je za određivanje površinske gustoće naboja koloidnih čestica. Dobiveni rezultati u skladu su s rezultatima klasične kiselinsko-bazne titracije koloidne suspenzije. Prednost je masene titracije u tomu što nije potrebno titrirati vodenu otopinu bez koloidnih čestica, već se prah kovinskog oksida dodaje u elektrolit poznatog pH. Da bi se odredila površinska gustoća naboja u cijelom pH području potrebna su dva pokusa.