

Interaction between oxalic acid and titania in aqueous ethanol dispersions

Per Dahlsten, Jarl B. Rosenholm*

Laboratory of Physical Chemistry, Center of Excellence for Functional Materials, Åbo Akademi University, FIN 20500 Åbo (Turku), Finland

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ABSTRACT

The charging effects resulting from adsorption of oxalic acid and oxalate anions on titania (anatase) surfaces in anhydrous or mixed water–ethanol suspensions is summarized. The suddenly enhanced electrical conductance with respect to titania free solutions has previously been explained in terms of surface-induced electrolytic dissociation (SIED) of weak acids. A recently published model has previously been found to successfully characterize the complex SIED effect. The model is evaluated experimentally by recording the conductance and pH of the dispersion and the zeta potential of the particles. The experimental results can be condensed to master curves, which reveal the major properties of the systems and facilitate further modeling of extensive experimental results. The equilibrium and transport properties of solutions and particles were related, but different mechanisms were found to be active in each case. The results suggest that at least three adsorption equilibria should be considered in order to improve the model.

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1. Introduction

In any systematic analysis of charging effects, no ion should be considered as naked in the solvent. Instead, all surfaces and ions are solvated, and adsorption occurs if the affinity of the adsorbate to the surface sites is greater than the solvation of the surface and adsorbate [1,2]. The Brønsted acid (proton donor) ability has been ascribed to strained oxygen bridges resulting from two adjacent hydroxyl ions, to be the active center. The Lewis acidity (electron acceptor) ability has been assigned to exposed coordinately unsaturated metal ions. The surfaces may also exhibit Lewis basicity (electron donor) properties. The hydroxyl groups at the metal oxide surface exist, as a function of increasing site density as single-, germinal- geminal- and hydrogen-bonded groups. The balance between Brønsted and Lewis type of surface sites can be adjusted by heat treatment, which influences the solvation of the powder [3].

In 1996, the mutual influence of monovalent alkali metal cations as well as some anions on TiO_2 (anatase) in aqueous suspensions was reported [4,5]. Later, the investigation was extended to charge interactions of multiprotic acids ($\text{H}_2\text{C}_2\text{O}_4$, H_3PO_4 , H_2SO_4) with colloidal (TiO_2 , Al_2O_3 , Fe_2O_3) particles in low-dielectric suspensions, such as alcohol (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_3\text{H}_7\text{OH}$)–water mixtures [6–11]. In alcohol-rich suspensions, the acids reside mainly in molecular form. Typically, the dissociation constant of a weak

acid in alcohols is lower by 2–4 orders of magnitude than in water. In alcoholic solutions of multiprotic acids, the concentration of pre-existing ions is therefore expected to be low.

In nonaqueous and aqueous alcohol suspensions, the surface of alumina has been found capable of catalytically dissociate ethanol adsorbing ethoxide anions on Lewis acid surface sites and protons on Lewis base surface sites [12]. Since ethoxide anions may desorb into the ethanol solvent, the surface is rendered a positive surface charge. In the presence of dissolved multiprotic acids, adsorbed surface complexes may form and induce a dissociation of solvated protons to the solution. This enhanced proton release is observed as an enhanced conductivity and a charge reversal denoted surface-induced electrolytic dissociation (SIED) [6–11]. It is opposite to the “normal” behavior when adsorption ionic species reduce the conductivity of the suspension resulting in charge neutralization [6–12]. Thus, the measured conductivity and charging of dispersions may be enhanced or depressed as result of two processes acting in opposite directions.

The aim of this report is to reevaluate some of our results published previously [6–11] by intercorrelating the key parameters characterizing ionic interactions in mixed and nonaqueous suspensions. Since the conductivity of proton is substantially higher than of other ionic species, the conductivity is expected to be directly proportional to the presence of protons in the suspensions. The potentiometrically determined pH represents the release of protons and may be converted to proton concentration (activity). The effective surface charge (ζ -potential) is dependent on the proton exchange at the surface hydroxyl sites. Moreover, a surface

* Corresponding author. Address: Laboratory for Physical Chemistry, Åbo Akademi University, Porthansgatan 3-5, FIN 20500 Åbo (Turku), Finland. Fax: +358 2 2330228.

E-mail address: jrosenho@abo.fi (J.B. Rosenholm).

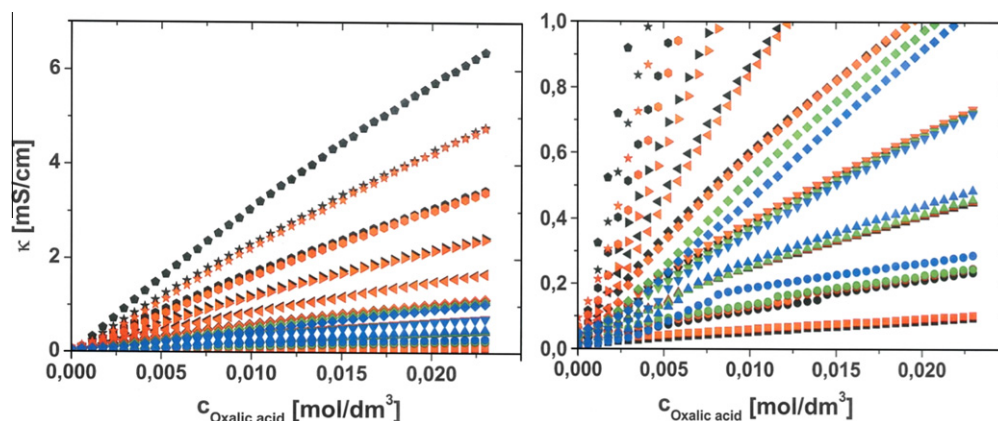
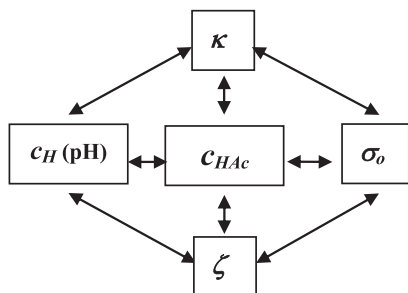


Fig. 1. Conductivity of titania–ethanol–water mixtures as a function of oxalic acid concentration at 25 °C. Left – full conductivity scale. Right – expanded conductivity scale. Symbols; square – 10%, circle – 20%, triangle – 30%, inverted triangle – 40%, diamond – 50%, left arrowhead – 60%, right arrowhead – 70%, hexagon – 80%, star – 90%, pentagon – 100% by weight water and for low-to-high conductivity to – 1%, – 2%, – 5%, – 10% titania (anatase) by weight at low water content. The reverse relationship applies for high water content.

charge density calculated from the proton concentration represents the true charging (potential) at the particle surface. Experimentally, the following four interlinked properties are thus recorded or calculated.



Conductivity is a measure of ion (proton) and zeta (ζ) potential a measure of particle transport in an external field. On the other hand, proton concentration and particle surface charge density (σ_o) are equilibrium properties. In order to highlight the key relationships, the extensive experimental material was reduced to 1–10 wt.% titania–94 wt.% ethanol–oxalic acid suspensions.

2. Experimental

Aeroxide (P-25) from Degussa was used as obtained. It is a relatively pure anatase (with admixture of rutile), and it consists of particles 30 nm in diameter with a specific surface area of 50 m²/g. The pristine pH_{iep} in aqueous solutions is about 6.5. Water was freshly obtained from a MilliQ device. Ethanol (94 wt.%) was supplied by Altia, Finland. Oxalic acid dehydrate (>99.5 %) was delivered by Fluka.

Acoustosizer IIs (Colloidal Dynamics, Warwick, USA) with a built-in pH-meter, conductivity meter, and thermometer was used to measure the pH, conductivity, and electrokinetic potential in dispersions containing 1–10 % of titania by mass. All solid-to-liquid ratios in this paper are expressed in terms of mass fractions. The instrument was used in “polar solvent” mode for aqueous dispersions and in “nonpolar solvent” mode for organic dispersions. A flow-through system and vigorous stirring were used to prevent sedimentation, and the dispersions were thermostated at 25 ± 1 °C. The instrument was kept in a fume hood. An external thermostat was used to keep the solutions and dispersions at 25 °C. Data points were taken in titration mode every 2 min, and 4 mL of titrant solution was added in 40 equally spaced portions

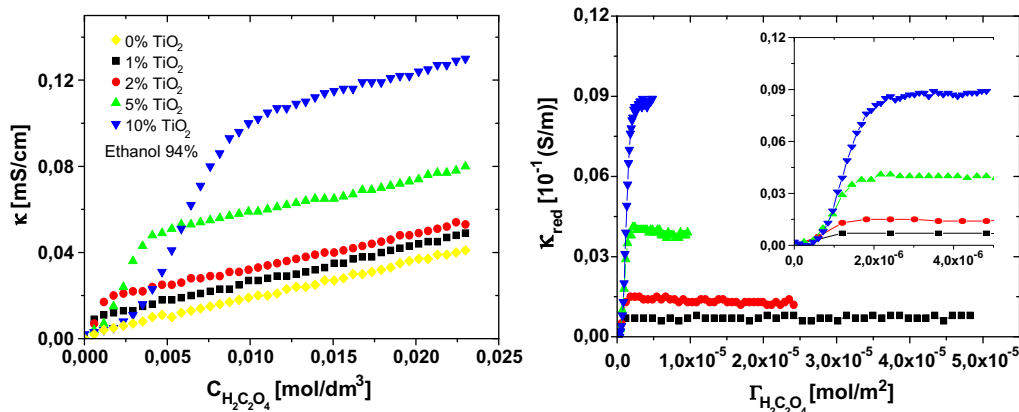


Fig. 2. The conductivity of 94% by weight ethanol TiO₂ (anatase) suspensions plotted as a function of oxalic acid concentration (left) and the reduced conductivity (right) plotted as a function of normalized oxalic acid concentration. Symbols; diamonds – 0%, squares – 1%, spheres – 2%, triangles – 5%, inverted triangles – 10% by weight TiO₂ (anatase) in 94% by weight aqueous ethanol suspensions at 25 °C.

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