



Historical Perspective

Influence of charge exchange in acidic aqueous and alcoholic titania dispersions on viscosity



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ARTICLE INFO

Available online 19 October 2015

Keywords:

Solvent/acid adsorption
 Solvent/acid dissociation
 Surface-induced dissociation (SIED, SILD, SIAD)
 Charge exchange
 Dispersion stability

ABSTRACT

Charging effects resulting from adsorption of acid, acid anions, and protons on titania (anatase) surfaces in anhydrous or mixed alcohol–water dispersions is summarized. The suddenly enhanced conductivity as compared to titania-free solutions has previously been modeled and explained as surface-induced electrolytic dissociation (SIED) of weak acids. This model and recently published results identifying concurrent surface-induced liquid (solvent) dissociation (SILD) are evaluated with experimentally determined conductivity and pH of solutions, zeta-potential of particles, and viscosity of dispersions. Titania (0–25 wt%)-alcohol (methanol, ethanol, and propanol) dispersions mixed with (0–100 wt%) water were acidified with oxalic, phosphoric, and sulfuric acids. It was found that the experimental results could in many cases be condensed to master curves representing extensive experimental results. These curves reveal that major properties of the systems appear within three concentration regions were different mechanisms (SILD, surface-induced liquid dissociation; SIAD, surface-induced acid dissociation) and charge rearrangement were found to be simultaneously active. In particular, zeta-potential – pH and viscosity – pH curves are in acidified non-polar solvents mirror images to those dependencies observed in aqueous dispersions to which hydroxyl is added. The results suggest that multiple dispersion and adsorption equilibria should be considered in order to characterize the presented exceptionally extensive and complex experimental results.

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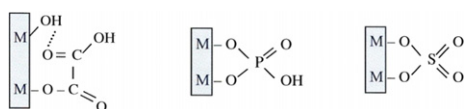
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1. Introduction

Solids can exist in different crystal forms which may catalyze chemical reactions and chemisorb solvent molecules and ionic species. Whereas oxide surfaces may act as ligands for cations in solution, the specific adsorption of anions or weak acids occurs by substitution of hydroxyls on the oxide surface. The effect of multivalent anions on the surface charging is sparsely investigated. Chelating acids such as oxalate, phosphate, and sulphate may replace mono-coordinated groups on the surface, which in aqueous dispersions is exhibited within $3 < \text{pH} < 4$ [1,2]. Obviously, this is the optimum pH-range for anion adsorption in aqueous solutions. The reactivity of surface hydroxyl groups toward anion substitution decreases as the acid character of these groups increases. Doubly and triply coordinated metal hydroxyls are more acidic and carry negative charges which do not favor electrostatic attraction with anions. The symmetry of anion charge plays an important role in its adsorption and its mode of coordination. Specific adsorption of anions is a surface complexation reaction and, as a rule, anions do adsorb more efficiently if their complexing nature is high in solution. In addition, these groups form bonds with surface cations that are more covalent in nature than the bonds formed with mono-coordinated hydroxyl groups. Their replacement is therefore more difficult. The chelating or bridging effect, which reinforces the complexing nature of the anion in solution, also stimulates adsorption [1,2]. The adsorption is dependent on whether anion affinity for the surface is greater than solvation of the surface or the acid anion [3,4]. In aqueous dispersions, the adsorption is predominated by charge neutralization, Brønsted acid–base and hydrogen bond interaction. The role of Lewis acid–base and van der Waals interaction is enhanced when the water content is reduced. Chelation may lead to a considerable increase of surface element dissolution (extraction).

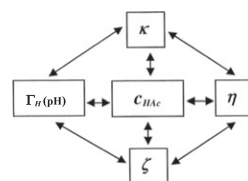
Oxalate anions adsorb through condensation with surface hydroxyl groups, but also via hydrogen bonding to the carbonyl groups [1,2]. Both the adsorption to mono-dentate surface complexes and the free carboxylic acid group enable a proton release. This effect seems to be specific to surface coordination because it is not observed with mononuclear complexes in aqueous solution. The dissociation constants of oxalic acid in water are [5] $\text{p}K_1 = 1.25$ (1.1), $\text{p}K_2 = 4.29$ (4.0), the value in parenthesis representing an ionic strength of $\text{p}I = 1$ (0.1 mol/dm³). Oxalate replaces mono-coordinated hydroxyl groups on the surface, but seems in some cases to be capable to chelate also doubly and triply coordinated hydroxyl groups [1,2]. Phosphate and sulfate replace mono-coordinated groups on the surface and possess a bridging coordination mode at around $3 < \text{pH} < 4$. For phosphate, this is only slightly more than the first dissociation constant of phosphate in water ($\text{p}K_1 = 2.15$, $\text{p}K_2 = 7.21$, $\text{p}K_3 = 12.34$) [5]. Sulfate anions are usually doubly coordinated on hydroxylated surfaces due to complexation. Since the acid constants of sulfate is very low in water ($\text{p}K_1 = -3$, $\text{p}K_2 = 1.94$) [5], both protons are dissociated. However, due to bi-dentate surface complexation, two hydroxyl groups are consumed. As a result sulfate only neutralizes surface charges at hydroxylated surface sites. The charging is obviously dependent on both pH (acidity) and pI (ionic strength). Only the mono-coordinated hydroxo groups are replaced. Phosphate replaces all mono-coordinated groups on the surface because it is a strong complexant [1]. Only one hydroxyl group remains active for excess charging upon adsorption.



We have previously reported on the mutual influence of metal cations as well as some anions on SiO₂, TiO₂, ZrO₂, Al₂O₃, Fe₂O₃, CaCO₃, and some other particles in aqueous dispersions [1,6–49]. Moreover, investigations on charge interactions of multiprotic acids (H₂C₂O₄, H₃PO₄, H₂SO₄) with such colloidal particles in low-dielectric suspensions, such

as ionic liquids [50–54] have been made. Properties of hydrocarbon [55–57] and alcohol (CH₃OH, C₂H₅OH, C₃H₇OH)–water dispersions [58–63] have been published. It was concluded that acids reside in alcohol-rich suspensions mainly in molecular form. This is due to order of magnitude reduced dissociation. For example, the acid constants of oxalic acid are shifted from $\text{p}K_1 = 1.25$, $\text{p}K_2 = 4.29$ in water to $\text{p}K_1 = 4.2$, $\text{p}K_2 = 8.2$ in anhydrous ethanol [58–63]. The $\text{p}K_i$ are depressed as the dielectric constant of the solvent decreases, e.g. as a function of the alcohol chain length. Due to the reduced ionic character the solubility of oxalic acid is enhanced almost two times to 2.07 mol/dm³. In alcoholic solutions of multiprotic acids, the concentration of preexisting ions is therefore expected to be low. In the presence of dissolved multiprotic acids, adsorbed surface complexes may form and induce a dissociation of solvated protons or anions to the solution. The enhanced proton release is observed as an enhanced conductivity and a charge reversal denoted surface-induced electrolytic dissociation (SIED) [58–63]. It is opposite to the “normal” reduction in conductivity in the presence of particles due to adsorption of protons and anions. Thus, the measured conductivity and charging of dispersions may be enhanced or depressed as a result of two processes acting in opposite directions.

The aim of this report is to review and extend some of our results published previously [58–63] by inter-correlating key parameters characterizing ionic interactions in mixed and non-aqueous methanol, ethanol, and propanol suspensions. Titania dispersions serve as model systems. Moreover, the influence of water as a mixed solvent is of particular interest. Since the conductivity of proton is substantially higher than other ionic species, the conductivity has been assumed to be directly proportional to the presence of protons in titania suspensions. The potentiometrically determined pH represents, however, the true proton concentration (activity) in bulk solution/suspension. This enables calculation of surface proton excess concentration and surface charge density which represent the charging (potential) at the particle surface. The effective surface potential (ζ -potential) is dependent on the proton exchange at surface hydroxyl sites. Finally, viscosity may be used to relate the effective surface charging to the stability of titania suspensions. Experimentally, the following four interlinked properties are measured 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, dispersed proton concentration and protons adsorbed to particle surface (surface charge density) are equilibrium properties. Obviously, the amount of adsorbed ions are interlinked to ζ -potential as particle properties while equilibrium proton concentration (pH) and conductivity are dispersion properties. Viscosity provides a mean to relate charge exchange to the overall suspension stability.

2. Surface chemistry model

In non-aqueous and aqueous alcohol suspensions, alumina surface has been found to catalytically dissociate adsorbed ethanol to ethanolate anions on Lewis acid surface sites and protons on Lewis base surface sites [64]. The assumption is that surface is Lewis or Brønsted active. The reaction occurs as a two-step process illustrated as the top reaction scheme in Fig. 1. First, ethanol adsorbs on the surface sites as neutral molecules and then ethanolate anions desorb from the surface into bulk dispersion. As a result, the surface is rendered a positive surface charge. The catalytic autoprotolysis of ethanol solvent on

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