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Stability of alumina suspensions in the presence of Tiron

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Abstract

The stability of alumina suspensions in the presence of Tiron was studied and discussed in the light of surface properties of alumina powder used, ionization chemistry of Tiron, and sedimentation behavior of the suspensions. The point of zero charge of alumina with and without addition of Tiron was determined using a batch equilibration method. The sedimentation of the suspensions was evaluated via screen sedimentation tests as a function of pH and Tiron concentration. The dissociation constant, pK_{a1}, of the hydroxyl groups of the Tiron molecule was determined by potentiometric titration carried out in water and KNO_3 as a background electrolyte. Tiron was shown to adsorb specifically onto the alumina surface in the examined pH range 4–10, but impart stability to the suspensions only at $pH \geq 6$.

Keywords: A. Suspensions; B. Surfaces; C. Chemical properties; D. Al_2O_3

1. Introduction

Colloidal processing of advanced ceramics has attracted increasing attention due to improved reliability and homogeneity control achievable by this approach. In general, preparation and transformation of a concentrated ceramic suspension of reasonably low viscosity are of key importance in all alternative wet forming methods [1–3].

Small organic electrolyte molecules with different functional groups have shown to be quite efficient in preparing stable aqueous suspensions of high solid loadings, as they do not build a steric barrier upon adsorption onto the particles. The effect of these dispersants is determined by both the number and type of ionisable groups and their adsorption behavior [4,5]. One of them is 4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt, commercially known as Tiron [3,6].

The aim of this work is to reveal in more detail the interaction of Tiron with the alumina surface and to characterize the effect of this molecule on the stability of aqueous alumina suspensions. Our previous study [7] has shown that Tiron adsorbs specifically in the whole experimental pH range 4–10 examined. The stability of suspensions with and without Tiron addition is studied and characterized in terms of point of zero charge of alumina, surface chemistry of Tiron, and sedimentation behavior of the suspensions.

2. Experimental

The used alumina powder (Alcoa CT 3000SG) had the following commercial characteristics: 99.7% α-Al_2O_3, $d_{50} = 0.6\ \mu m$, $Sp = 6\ m^2\ g^{-1}$. Tiron was produced by Aldrich. The point of zero charge of the alumina powder, pH_{PZC}, was determined by a batch equilibration method [8], using KNO_3 (10^{-2} mol/L) as a background electrolyte. Tiron was added in a quantity from 0 to 10 g/L, i.e. 0–10% expressed on dry weight basis (dwb) of alumina. The stability of suspensions was evaluated via screen sedimentation test. Series of samples containing 5 g Al_2O_3/50 mL KNO_3 solutions with different pH values, were shaken mechanically in PVC vessels for 24 h, poured into graduated cylinders (50 mL), and left to settle in a vibration-free environment. Suspension configuration change was monitored over a different period of time, i.e. when the change was noticeable. Surface chemistry of the Tiron molecule was studied by potentiometric titration.

3. Results and discussion

Immersion of a ceramic powder in water results in the buildup of a charge at the solid–aqueous interface. The association–dissociation reactions of amphoteric surface

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groups (MOH) on oxide ceramics can be written as [9]:

$$\text{MOH} \Leftrightarrow \text{MO}^- + \text{H}^+ \quad (1)$$

$$\text{MOH}_2{}^+ \Leftrightarrow \text{MOH} + \text{H}^+ \quad (2)$$

A point of zero charge (PZC) is the pH value where $[\text{MO}^-]$ and $[\text{MOH}_2{}^+]$ surface concentrations are equal, i.e. surface charge, $\sigma_0 = 0$. The surface charge is negative at $\text{pH} > \text{pH}_{\text{PZC}}$ and positive at $\text{pH} < \text{pH}_{\text{PZC}}$. An isoelectric point (IEP) corresponds to the pH value where zeta potential is equal zero, $\xi = 0$. In the simplest case, if the specific adsorption of ions and dissociation of counterions are neglected, then pH_{PZC} coincides with pH_{IEP}.

The results obtained in this study for pH_{PZC} of the used Al_2O_3 powder, given as a dependence of the pH values of filtered KNO_3 solutions after 24 h equilibration with alumina, pH_f, on initial pH values, pH_i, are presented in Fig. 1. The plateau obtained at pH 8.3 corresponds to the point of zero charge of as-received powder. The influence of Tiron addition on the pH_{PZC} is also illustrated in Fig. 1. As can be seen, Tiron adsorbs specifically onto the alumina surface; moreover, its presence causes a shift in the pH_{PZC} value in two opposite directions. Namely, depending on the initial pH values of electrolyte, formation of two distinct plateaus is revealed. For the pH_i values ranging from 2 to 8, a plateau descends towards lower pH_f values, whilst, in the interval of basic pH_i ($\text{pH}_\text{i} > 8$) the other mounts towards higher pH_f values in comparison with those of the as-received powder. This trend becomes more pronounced with increasing Tiron concentration. In acidic region ($\text{pH}_\text{i} < \text{p}K_{\text{a1}}$) the amount of Tiron ranging from 0.1 to 10% dwb causes a pH_{PZC} shift from 8.2 to 5.8, respectively, i.e. total shift, $\Delta\text{pH}_{\text{PZC}}$, equals 2.5 pH units. In basic region ($\text{pH}_\text{i} > \text{p}K_{\text{a1}}$) $\Delta\text{pH}_{\text{PZC}}$ is 1.1.

There are no literature data about the influence of Tiron on the pH_{PZC} value of alumina. Numerous authors [6,10–12] studied the change of its IEP in the presence of Tiron. The pH_{IEP} of aluminas of different suppliers varied from 7.5 to 9. It is worth noting that for Alcoa sample the pH_{IEP} equaled 8.1, which accords well with pH_{PZC} of 8.3 obtained for Alcoa CT 3000 alumina used in this study. Depending on the amount of Tiron added, the registered pH_{IEP} shifts from 3 to 6 pH units towards the acidic values [6,10–12].

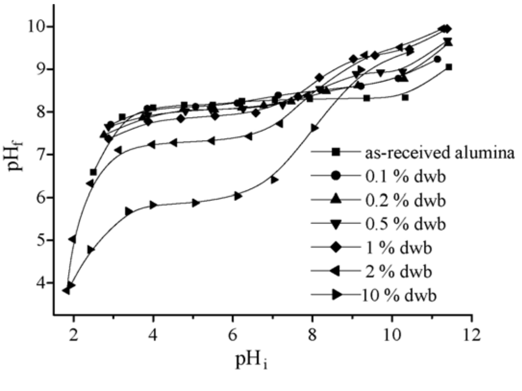

Fig. 1. Influence of Tiron addition on pH_{PZC} of as-received alumina.

The results are in good agreement with the ones presented in this study, as it is known that pH_{IEP} and pH_{PZC} exibit different shifts in respect to the ionic species adsorbed specifically onto the surface. Namely, anions cause a shift of pH_{IEP} and pH_{PZC} towards lower and higher pH values, respectively, unlike cations which presence initiates an opposite move. Thus, it is reasonable to conclude that the registered shifts of pH_{PZC} indicate specific sorption of different ionic species of Tiron from the solution. In basic region, Tiron dissociates and adsorbs as negatively charged ion. In acidic region, it adsorbs most likely in a protonated form or as uncharged molecule.

As Tiron is a weakly acidic electrolyte dispersant, its ionization behavior was studied by a potentiometric titration, carried out in water and KNO_3 (10^{-2} mol/L) as a background electrolyte. As expected, the curves obtained using water and electrolyte are quite similar, with a slight trend towards an increased ionization in the presence of KNO_3, Fig. 2a. More importantly, the curves show that Tiron is essentially uncharged below pH 6, and fully ionized above pH 10. According to the first derivatives for water and electrolyte solution, Fig. 2b, dissociation constants, $\text{p}K_{\text{a1}}$, of OH groups were determined to be 7.8 and 7.6, respectively. The result accords well with the literature data [10,13] with close numeric values of about 7.60

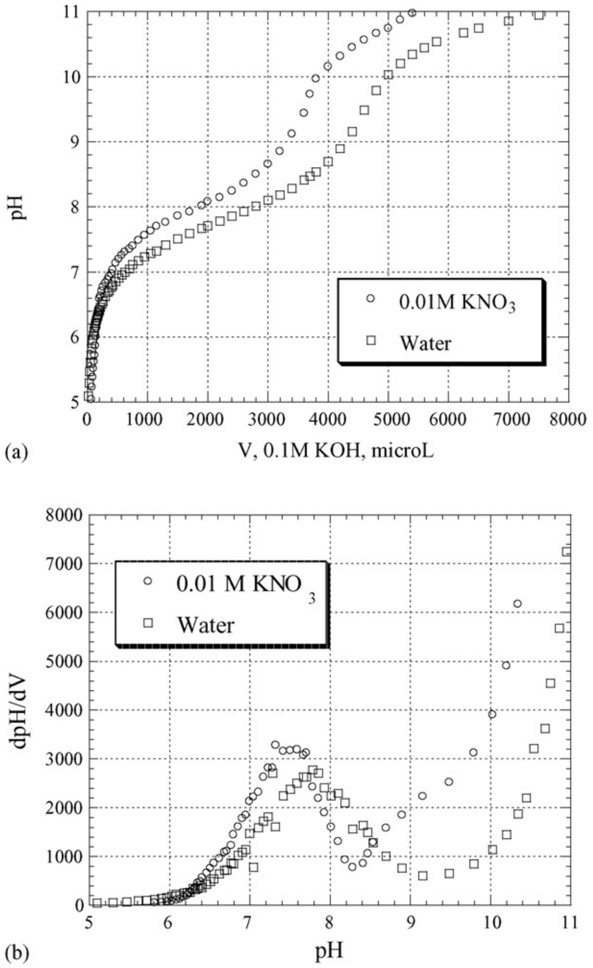

Fig. 2. Potentiometric titration of Tiron in water and electrolyte (a) and first derivative (b) curves.

and 12.50 for the first and the second dissociation constants of Tiron. Gao [14], however, reported somewhat higher values; $pK_{a1} = 8.31$, and $pK_{a2} = 13.07$.

Stability of alumina suspensions over different pH values, without and with Tiron addition, was compared and judged via sedimentation velocities, expressed as a change in suspension height with time, Fig. 3. The suspension height was calculated by subtracting the top interface height that separated supernatant from the rest of the suspension.

In the vicinity of $pH_{PCZ,}$ suspensions in the absence of Tiron settled completely within first 20 min, as the alumina particles were subjected to the strongest attraction without electrostatic repulsion from the surface charge. It is known that alumina can be well dispersed in water if the suspension pH is at least two units away from the point of zero charge. In our case, at $pH \approx 10$, the suspensions still settled very fast. Suspension preparation was attempted in acidic region and electrostabilization around pH 4 imparted stability over a days long period of time. Contrary to our expectations, because it was shown before that Tiron adsorbs preferentially at acidic and neutral pH [7,10] which excellently correlates with the ΔpH_{PZC} results in this study, its addition led to the destabilization of acidic suspensions, Fig. 3a. The suspension settled quickly, within 60 min, forming a voluminous sediment. The more acidic pH′, the faster the velocity. As particles settled, they left behind a clearly discernible interface from the supernatant. An increase of dispersant concentration had no positive impact on the suspension stability. Quite opposite effect was obtained upon Tiron addition at $pH' \geq 6$, as suspensions exhibited a rather slow settling rate, Fig. 3b. Appearance of different concentration zones was registered along the cylinders height: top clear, zone of graduated turbidity and sediment, as suspensions turned from flocculated to the rather stable ones. Suspension stability was not remarkably enhanced by doubling the Tiron concentration.

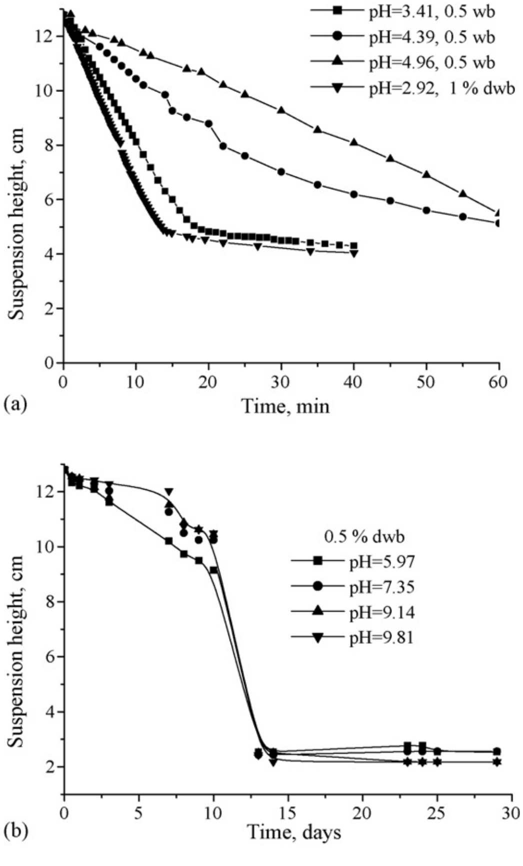

Fig. 3. Change in alumina suspension height with time in presence of Tiron: (a) acidic and (b) basic region.

By combining titration and pH_{PZC} results, an interpretation of the suspension stability can be given. As shown, in acidic pH region, as $pH < pH_{PZC}$ (which also coincides with pH below pK_{a1} of Tiron) free surface hydroxyl groups of alumina are protonated, so repel each other and stabilize the suspension. Addition of Tiron led to an instantaneous destabilization. Over the pH range 6–10, the suspension stability was improved in the presence of Tiron. According to the potentiometric data, dissociation of the hydroxyl groups of Tiron starts in this region, giving an additional contribution to the overall negative charge of the molecule. For this reason, an electrostatic repulsion between Tiron and alumina would be expected to occur, especially in the region of high negative charge of Al_2O_3 particles ($pH > pH_{PZC}$) leading to suspension destabilization. However, this was not the case.

According to [3,10,13], the adsorption of Tiron in the alkaline region proceeds via specific interactions, i.e. an inner sphere complex is built between alcohol groups of the molecule and hydroxyl groups of alumina. A strong repulsive interaction between the alumina particles is created via negatively charged sulfonate, $-SO_3Na$, groups imparting stability to the suspension. This approach is well supported by authors [4] who state that an electrolyte could be an efficient dispersant if functional groups, which permit a strong adsorption, are different from those functionalities which create the surface charge.

The effect of pH on suspension stability was also confirmed via differences in rheological behavior, Fig. 4. It is clearly seen that suspensions at $pH \geq 6$ exhibit almost the same slight shear thinning behavior. Significant increase in suspension viscosity with pH decreasing, agrees well with the opposite pH_{PZC} shifts and corresponding sedimentation behavior found in acidic and basic pH region.

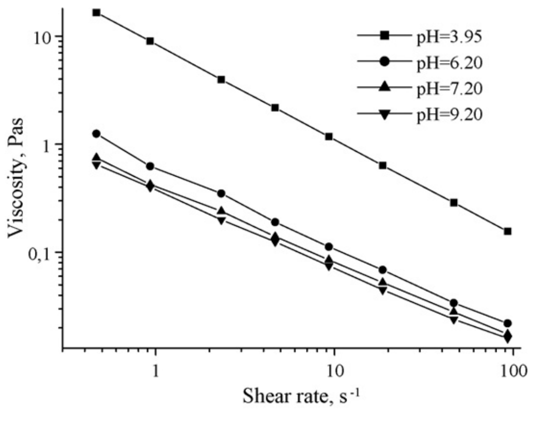

Fig. 4. Viscosity vs. shear rate of the 60 mass% suspensions as a function of pH (1.5% dwb Tiron added).

4. Conclusions

Point of zero charge of the alumina powder, determined by a batch equilibration method, using KNO_3 (10^{-2} mol/L) as a background electrolyte is 8.3. The Tiron addition, as a function of initial pH values, causes a shift in the pH_{PZC} value in two opposite directions, indicating specific adsorption of different ionic species of Tiron. The ionization constant, pK_{a1}, of the Tiron molecule, determined by the potentiometric titration, in water and KNO_3, equals 7.8 and 7.6, respectively. It was shown that Tiron imparts stability to the aqueous alumina suspensions at $pH' \geq 6$.

Acknowledgements

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