Adsorption of itaconic acid from aqueous solutions onto alumina

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Abstract: Itaconic acid, IA ($C_5H_6O_4$), was investigated as a potential flocculant for the aqueous processing of alumina powders. The adsorption of IA, as a function of its concentration and pH value of the solution, onto the alumina surface was studied by the solution depletion method. The stability of the suspensions in the presence of itaconic acid was evaluated in light of the surface charge of the alumina powder used, the degree of dissociation of IA, as well as the sedimentation behavior and rheology of the suspensions. It was found that the adsorption process is extremely pH dependent; the maximum adsorption of IA onto alumina surface occurring at a pH close to the value of the first IA dissociation constant, pK_{a1}. Also, IA does not influence the value of the point of zero charge of alumina. It was shown that IA represents an efficient flocculant for concentrated acidic alumina suspensions.

Keywords: alumina; itaconic acid; adsorption; stability; flocculation; suspension.

INTRODUCTION

The preparation and transformation of concentrated aqueous ceramic suspensions are of paramount importance in the manufacture of ceramic parts. The key element in the colloidal processing of ceramic powders is maintaining control over the interparticle forces within the suspension during all stages; certain steps depend on repulsive forces between the particles, whereas other steps may require attractive ones.[1–3] Stable suspensions can be prepared if the repulsive potential between the particles is of sufficient magnitude that the attractive van der Waals potentials are counterbalanced or exceeded. The consolidation stage can be very slow due to the high fluidity of suspensions; and the formed green body can be rather brittle and difficult to handle. Many methods have been developed in recent years to improve ceramic processing by transforming the homogeneous suspension into a near net-shaped solid green body. This can be achieved either by

consolidating the dispersion medium as in gel casting,[4] or by flocculating or coagulating the powder particles in suspension, *i.e.,* direct coagulation casting, *etc*.[5–7]

Polymers can induce either stabilization or flocculation of the suspension, depending on many factors, such as the nature of the particle surface, chemical structure and concentration of the polymer, dispersion medium, *etc*.[8–9]

Numerous and different kinds of organic molecules, *i.e.*, dispersants, have been used to prepare stable ceramic suspensions. Contrary to other adsorbing polymers having a charged species at only one end of the molecule, polyelectrolytes possess a charge that is present along the length of the chain, imparting electrosteric stabilization.[10,11] The use of small electrolyte molecules has gained in interest, as they enable the preparation of high solid content suspensions without a steric barrier. Their efficiency is determined by their ability to be adsorbed onto the powder surface and by a large number of functional groups which can dissociate and act as surface charge modifiers.[12] Graule *et al*.[1] investigated the potential of phenols and low-molecular aromatic carboxylic acids as alumina dispersants. A number of aliphatic organic acids were tested to study the effect of chain length, localization of double bond, number of –COOH groups, *trans/cis* isomery, *etc*., on the stability of Al_2O_3 suspensions.[13]

Non-adsorbing polymers usually induce depletion flocculation, or phase separation, but if added in larger concentrations they lead to depletion (re)stabilization. In the case of adsorbing polymers, different types of effects can be identified. If one polymer molecule adsorbs more than one particle simultaneously, then the polymer holds the particles together. This effect is called bridging flocculation and is usually a result of strong adsorption of low concentrations of high molecular weight polymers. If, instead, the polymer forms a layer on each particle, this can lead to a repulsive force, *i.e.*, steric stabilization. However, if the adsorbed layer is thin, the effect of short range van der Waals attraction may lead to weak flocculation and the suspension becomes more viscous. When a polyelectrolyte of opposite charge to that of the particles is added, flocculation occurs by charge neutralization.[8,9]

Itaconic acid (IA), $C_5H_6O_4$, (3-carboxy-3-butanoic, propylenedicarboxylic acid), is an unsaturated dicarbonic acid. IA is soluble in ethanol, acetone and water; it dissociates in aqueous solutions (pK_{a1} = 3.85 and pK_{a2} =5.55).[14] It is a small molecular weight monomer, obtained by distillation of citric acid (CA). CA and its salts are commonly used as alumina dispersants. However, unlike citric acid, IA does not possess any additional functionality, which would contribute to the charging of the alumina particles.

IA is an environmentally friendly substance with a large variety of industrial applications, *e.g*., as a comonomer in resins and in the manufacture of synthetic fibers, coatings, adhesives, thickeners and binders.

The intent of the present work was to investigate the efficiency of itaconic acid as a potential flocculant for the aqueous processing of alumina. The interactions of IA and alumina surface were studied in more detail to characterize the effect of this molecule on the stability of Al_2O_3 suspensions. The adsorption of IA was studied as a function of its concentration and solution pH. The suspension stability with and without IA addition was studied and evaluated in terms of the point of zero charge of alumina, the ionization chemistry of IA, and the sedimentation behavior and rheology of the suspensions.

EXPERIMENTAL

Alpha-alumina (CT 3000 SG) with an average particle size of $d_{50} = 0.6$ μm and a BET specific surface area, $S_p = 6$ m^2 g^{-1}, was produced by Alcoa, Germany. The itaconic acid was purchased from Aldrich-Chemie. The adsorption behavior of IA onto alumina was studied using a batch method. Fractions of alumina (5.0 g) were added to separately prepared 50 ml KNO_3 solutions of set pH values (initial, pH_i values) with different amounts of IA, up to 0.20 g l^{-1}. PVC vessels containing the samples were agitated mechanically for 24 h at room temperature. High-speed centrifugation allowed the separation of the supernatant for analysis. The quantity of IA adsorbed was determined by the solution depletion method, using UV spectrophotometry (Uvicon 810/820, Kontron Instruments, Austria). In order to assess quantitatively the amount of IA remaining in the supernatant, calibration curves were constructed for each measurement, *i.e.*, each pH after 24 h of equilibration, pH_e. The absorbance of IA solutions was recorded in the range from 190 to 330 nm. The calibration curves were obtained from the absorbance at the wavelength of maximum absorbance, 242 nm. The calibration is linear for the IA concentration range from 0 to 0.14 g l^{-1} for all pH_e values. The point of zero charge of alumina with and without the addition of IA was also determined by applying the batch equilibration method.[15] The suspension stability at different pH, with and without IA, was evaluated *via* gravity sedimentation tests, by pouring 50 ml of the given suspension into a graduated glass cylinder. The sediment heights were recorded as a function of time. The viscosity of the suspensions was measured using a Brookfield Synch instrument.

RESULTS AND DISCUSSION

Adsorption of itaconic acid onto α-Al_2O_3

The adsorption of IA onto alumina was studied in the pH_e interval from 3.00 to 8.50. Adsorption isotherms obtained for the suspension with pH_e set at 3.85 and 3.15, *i.e.*, at pH ≤ pK_{a1}, are presented in Fig. 1. The related adsorption curves, given as the dependence of the adsorbed amount of IA per g of alumina *vs.* the IA equilibrium concentration in the supernatant,[16] were constructed based on the difference between the initial IA concentration, c_0, and that remaining in the supernatant, c_e, according to the mass balance in the batch:

$$\Gamma = \frac{V(c_0 - c_e)}{m} \tag{1}$$

where: Γ is the amount of adsorbed IA (g_{IA} $g_{alumina}^{-1}$), m (g) the amount of alumina powder and V (ml) the volume of the solution.

Although the adsorption of IA at both the examined pH values increased with increasing IA concentration until a plateau was attained, the shape of the curve obtained at pH_e 3.15 indicates a rather small amount of IA adsorbed. However, the given isotherm exhibits at pH_e 3.85 a much steeper initial slope, with a plateau attained at a much higher level, indicating the greater affinity of itaconic acid for α-Al$_2$O$_3$ surfaces at $pH_e = pK_{a1}$. After 24 h, about 60 % of the initial amount was adsorbed.

The effect of the different pH_e values studied on the amount of IA adsorbed onto the alumina is summarized in Fig. 2. The observed differences in adsorption will be discussed later in the text.
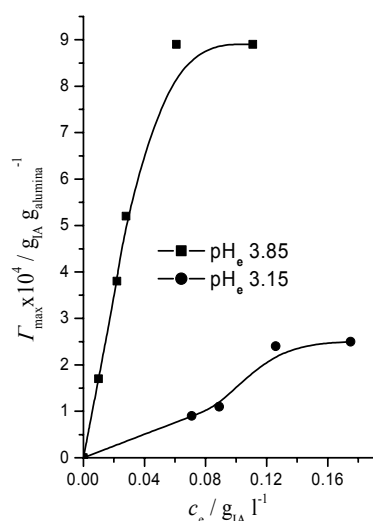

Fig. 1. Adsorption isotherms of itaconic acid onto alumina at various pH_e values.
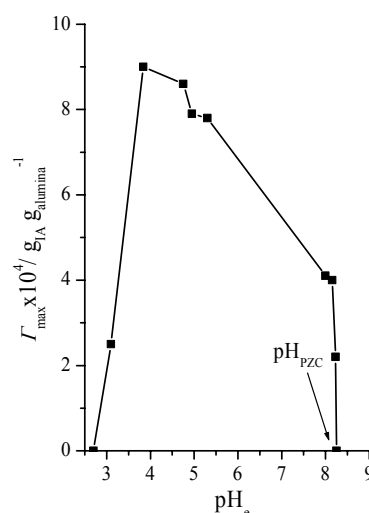
Fig. 2. The adsorption of itaconic acid as a function of suspension pH_e.

The effect of the addition of IA on the pH_{PZC} of the alumina powder

It is well-known that the point of zero charge, pH_{PZC}, together with the iso-electric point, pH_{iep}, and the surface charge of the particles, σ_0, is an important guide to the interfacial properties of a ceramic powder. Following the approach of Davis *et al*. on the dissociation-association of the amphoteric surface groups present on alumina, the reactions that occur and cause particle charge at pH_s below and above pH_{PZC} can be defined by Eqs. (2) and (3), respectively:[17]

$$AlOH_2^+ \rightleftharpoons SOH + H_s^+ \qquad (2)$$

$$AlOH \rightleftharpoons SO^- + H_s^+ \qquad (3)$$

where $AlOH_2^+$, SOH, and SO$^-$ denote the positive, neutral and negative sites on an Al$_2$O$_3$ surface.

The result obtained for the pH_{PZC} of the as-received Al_2O_3 powder, given as the dependence of the pH value of filtered KNO_3 solutions after 24 h equilibration of the alumina, pH_f, on the initial pH values, pH_i, is presented in Fig. 3. The plateau observed at pH 8.3 corresponds to the point of zero charge of the investigated powder. This value is in good agreement with previous results.[18,19]
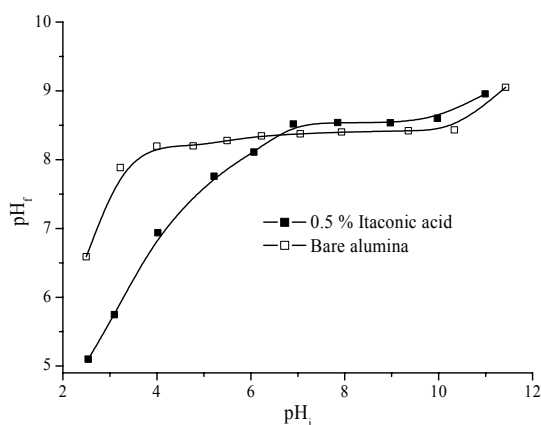

Fig. 3. Determination of the pH_{PZC} of alumina and the effect of itaconic acid addition on it.

The influence of IA addition on the pH_{PZC}, also evident from the dependence of pH_f *vs.* pH_i, was found to be somewhat different with respect to the interval of pH_i values, also presented in Fig. 3. In the range of pH_i values above pK_{a2}, *i.e.*, pH $\geq$ 6.00, the position of the plateau was unaffected by the presence of IA, indicating no specific IA adsorption onto alumina occurred. A change in the plateau length and shape was observed for $pH_i \leq 6.00$, *i.e.*, below the dissociation constant of IA. This can be explained either by the screening effect caused by the presence of IA, or by its non-specific adsorption onto the alumina surface. Consequently, the reaction responsible for the positive charging of alumina particles at $pH_s < pH_{PZC}$ was suppressed.

From the presented insight in the surface charging of alumina and taking into consideration the dissociation of itaconic acid ($pK_{a1} = 3.85$ and $pK_{a2} = 5.55$), the differences in IA adsorption, measured at various suspension pH_s, can be easily understood. It is evident, Fig. 2, that a maximum in the IA adsorption onto alumina occurs around pH 3.80, *i.e.*, close to the value of pK_{a1}. As the pH decreases, the positive charge of the alumina increases but the number of negatively charged IA sites continually decreases, leading to reduced (pH 3.15) or suppressed adsorption (pH 2.70). Still appreciable adsorption occurs at pH values near the value of the second dissociation constant. However, IA adsorption decreases with increasing pH, as the attraction between the positively charged alumina surface and the negatively charged IA anion decreases with increasing pH, becoming negligible in the vicinity of the pH_{PZC} value of alumina. At pH $>> pH_{PZC}$, no measurable adsorption occurs, confirming the mutual repulsion be-

tween the negatively charged adsorbent (alumina) and adsorbate (IA). This trend indicates the electrostatic mechanism of the adsorption process.

The result agrees well with the literature data.[13] Tomasik *et al.* confirmed the electrostatic nature of the adsorption mechanism for a series of aliphatic carboxylic acids onto alumina, including succinic acid.[13] It is worth noting that itaconic acid can also be regarded as methylene succinic acid.

Studart *et al.*[20] also claimed that the adsorption process is pH dependent, and significantly influenced by the dissociation constants (pK_a values) of the functional groups that constitute the adsorbing molecule. It was observed that the maximum adsorption occurred in a pH range near the pK_a values of the dissociating groups in the molecule. Less adsorption was expected to occur at pH $\leq$ pK_a due to the absence of dissociated anchoring groups on the molecule. At pH $\geq$ pK_a, although the functional groups are expected to be fully dissociated, the lower density of the positively charged sites on the alumina surface limits the adsorption of anionic molecules.[21]

Hidberg *et al.*[12] studied the adsorption of citric acid (CA) onto alumina powder over a wide pH range. The amount of CA varied from 0.1 to 0.6 wt. %. Almost complete adsorption was observed at pH values between 3.0 and 7.0, with values of 0.52 and 1.02 μmol CA m^{-2} Al$_2$O$_3$ measured for 0.1 and 0.2 wt. % CA, respectively. In general, with increasing pH, the adsorption of citric acid decreased. The maximum in the adsorption occurred at pH 3.0, a value close to the value of pK_{a1} of CA. The citric acid molecule has four functionalities: three COOH and one OH group (pK_{a1} = 3.13, pK_{a2} = 4.76 and pK_{a3} = 6.40).

In this study, the maximum adsorption of itaconic acid (0.20 wt. % IA added) was also registered at pH = pK_{a1}, with the value of 8.8 10^{-4} g IA/g Al$_2$O$_3$, *i.e.*, 1.13 μmol IA/m^2 Al$_2$O$_3$. Variation from this pH value had a negative impact on the adsorption process.

Contrary to itaconic acid, the adsorption of CA was also registered at pH values > pK_{a3}, which was attributed to the formation of an inner-sphere complex between the citrate ion and the alumina surface. This mechanism is most often described by the ligand (L)-exchange model,[22] where, in the case of CA, two COO$^-$ groups in the molecule participate in the complex formation, while the third one and the hydroxyl group contribute to an increase in the negative surface charge, thus leading to electrostability of alumina suspensions. However, unlike CA, IA has neither additional functionalities, which would render charge to the particles, nor a negative incremental charge, due to the presence of a double bond of sufficient magnitude to create a negative charge on the alumina particles upon adsorption.

Stability of alumina suspensions in the presence of IA

The stabilities of alumina suspensions with different pH values, both without and with IA addition, were compared and judged *via* sedimentation velocities,

expressed as the change in the suspension height with time, Figs. 4–7. The suspension height was calculated by subtracting the top interface height separating the supernatant from the rest of the suspension.

The alumina suspension prepared in the acidic region, around pH 4, exhibited stability over a long period of time, due to simple electrostability, as seen, Fig. 4. The addition of IA in an amount of 0.50 wt. %, did not significantly influence the stability. A slight decrease in acidity (pH 4.3) resulted in a faster particle settling, Fig. 5.
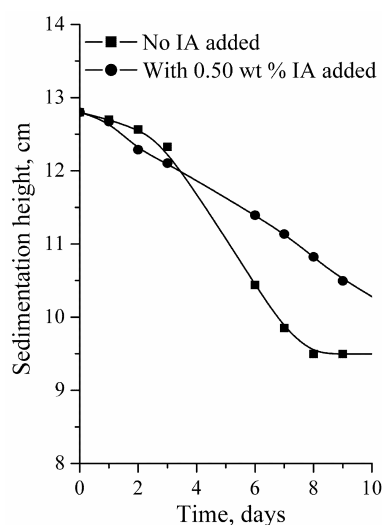
Fig. 4. Change in the alumina suspension height with time at pH 3.8 with and without IA addition.
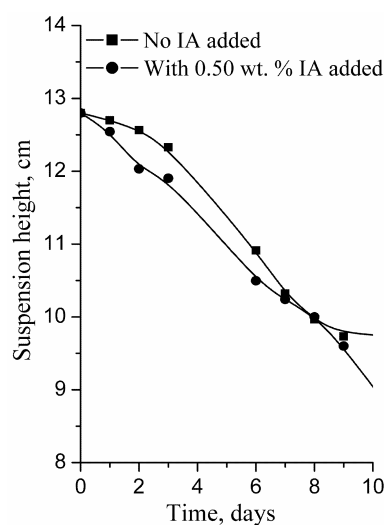
Fig. 5. Change in the alumina suspension height with time at pH 4.3 with and without IA addition.

The suspension stability at pH values above the second dissociation constant of itaconic acid, $pK_{a2} = 4.55$, is shown in Fig. 6. As can be seen, the stability decreased with increasing pH, so that at $\approx$ pH 6, the particles settled during one hour. More basic pH values promoted suspension instability. For comparison, the change of the suspension height with time with no IA added at pH $\geq$ pH$_{PZC}$ of Al$_2$O$_3$ is illustrated in Fig. 7. In the vicinity of pH$_{PZC}$, the alumina suspensions settled completely within the first 20 min, as the powder particles were subjected to the strongest attraction without electrostatic repulsion from the surface charge. A pH increase to pH 10.0 was not sufficient to impart stability to the suspension.

The flock diameters in suspensions prepared at pH > pK_{a2} were calculated using the experimental results (Figs. 6 and 7) and the Stoke law:

$$v = \frac{d^2 g(\rho - \rho_0)}{18\eta} \tag{3}$$

where d is the particle diameter, g the acceleration of free fall, ρ and ρ_0 the particle and liquid densities, respectively, and η the viscosity of the liquid.
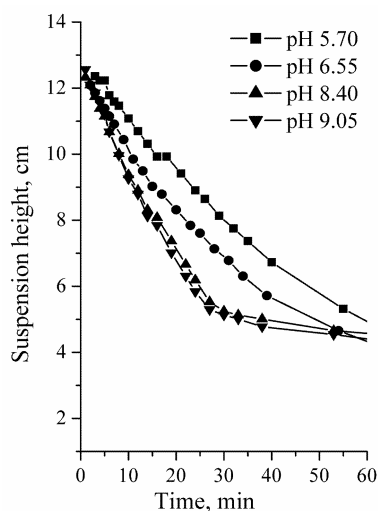

Fig. 6. Change in the alumina suspension height in time with 0.50 wt. % IA added.
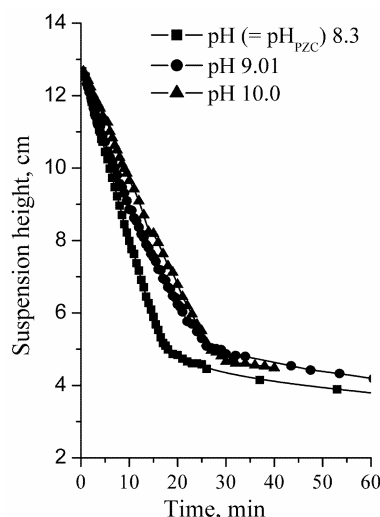
Fig. 7. Change in the alumina suspension height in time with no IA added.

The related flock diameters in the IA suspensions ranged from 4.25 to 5.0 μm at neutral pH values, while they were about 6 μm in the alkaline region. The flock diameters calculated for suspensions without IA at pH ≈ pH$_{PZC}$ were somewhat larger, probably due to the fact that in the presence of IA, the attraction of particles was screened and they settled slightly slower. The settling velocities were the same for both suspensions at pH 9.00, confirming that the addition of 0.50 wt. % IA to the dilute Al$_2$O$_3$ suspension at pH > pK_{a2} has no impact on its stability.

Rheological behavior of the alumina suspensions in the presence of IA

Alumina suspensions with a high solid content, 70 wt. %, were prepared without and with IA at pH 3.85, *i.e.*, at the pH where the maximum amount of itaconic acid was adsorbed. The low viscosity (< 4 Pa s, at a shear rate of 1.0 cm^{-1}) measured for the suspension without IA indicated that its stability was imparted *via* electrostabilization. The addition of IA in the amounts of 0.50, 1.0 and 1.5 wt. % led to an increase in the suspension viscosity, which was not possible to be measured by the available instrument. However, the suspensions appeared to be very smooth and paste-like, with no visible phase segregation. They easily regained fluidity upon the slightest addition of acid. Such behavior suggests that partially negatively charged IA molecules at pH 3.85 interact with positively charged alumina surface sites patch wise and flocculation occurs by charge neutralization.

To achieve further progress in the application of IA in gel casting or other near-net forming methods, a detailed study of the optimum surface coverage for flocculation, the influence of temperature, catalyst, effect of other monomer addition, *etc.*, is required for a clearer understanding of the flocculation mechanism and its potentialities.

A superior strength improvement in an acrylamide–IA system for the manufacture of paper was reported recently. The authors, who used this system in the presence of inorganic particles, also stated that an increase in the amount of IA increased significantly the water swelling, as well as the gel strength.[23]

CONCLUSIONS

The adsorption process of itaconic acid, IA, onto alumina, at various pH values, was investigated. It was found that the adsorption is strongly governed by the pH of the suspension and increases with increasing IA concentration. The maximum adsorption occurs at a pH close to the pK_{a1} of IA. At lower and higher pH values, the adsorption decreases, confirming its electrostatic mechanism. The pH_{PZC} of alumina was determined by the batch equilibration technique and was found to be 8.3. The presence of IA does not cause a shift in the pH_{PZC} value.

Sedimentation data showed that the addition of 0.50 wt. % IA has no significant influence on the stability of a dilute alumina suspension. However, the rheological behavior of concentrated (70 wt. %) suspensions confirmed that IA is very efficient in the flocculation of acidic (pH $\approx$ pK_{a1}) suspensions; the flocculation mechanism involved is charge neutralization.

И З В О Д

АДСОРПЦИЈА ИТАКОНСКЕ КИСЕЛИНЕ ИЗ ВОДЕНИХ РАСТВОРА НА АЛУМИНИЈУМ-ОКСИДУ

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Изучавана је примена итаконске киселине, ИК (C$_5$H$_6$O$_4$), као потенцијалног флокуланта, за водено процесирање прахова алуминијум-оксида. Адсорпција итаконске киселине на површини алуминијум-оксида изучавана је у функцији концентрације и pH раствора. Стабилност суспензија алуминијум-оксида у присуству итаконске киселине објашњена је узимајући у обзир површинско наелектрисање алуминијум-оксида, степен дисоцијације итаконске киселине, седиментационо понашање и реолошка својства суспензија. Нађено је да адсорпција ИК јако зависи од pH. Максимална адсорпција ИК на површини алуминијум-оксида дешава се при pH вредности блиској вредности прве константе дисоцијације ИК, pK_{a1}. Додатак итаконске киселине не утиче на вредност тачке нултог наелектрисања алуминијум-оксида. Показано је да је ИК ефикасан флокулант за концентроване, киселе суспензије алуминијум-оксида.

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