Interaction and stabilization of DMF-based alumina suspensions with citric acid

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ABSTRACT

The understanding of the detailed interaction between particles and dispersants in non-aqueous solutions is important for industrial applications. Herein, we report the investigation on the alumina suspension with citric acid in *N,N′*-dimethylformamide (DMF). The interaction was characterized by monitoring the evolution of UV–vis spectra, zeta potential values, and FT-IR spectra. The dispersion stability was examined by sedimentation test. It is found that the adsorption of citric acid on the surface of alumina particles depends on the apparent pH (pH$_a$) values of the solution. The adsorption follows the Langmuir type. The DMF-based alumina suspension exhibits a high stability due to the adsorption of citric acid on alumina particles, and shows the highest stability at pH$_a$ 2.6 where the maximum adsorption occurs for citric acid.

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1. Introduction

Ceramics are currently one of the most attractive materials for numerous applications such as in aerospace, automotive, vessels, biology, textile engineering, and chemical industry, due to their chemical and thermal stability, high strength and wear resistance [1–3]. Well-dispersed slurry is of importance to the ceramic industry processes such as direct coagulation casting, gel-casting, tape-casting, and injection molding [4,5], which can be achieved by the addition of certain dispersants that adsorbed onto the particles thereby increasing the interparticle forces to overcome aggregation. In the past decades, the stabilization of alumina in aqueous solution has been extensively studied [6,7]. However, there are a few drawbacks of using water to prepare high performance ceramics, especially for some functional materials, such as porous ceramics. The high surface tension of water directly brings on large capillary force in the solvent removing process, resulting in a considerable irreversible shrinkage accompanied by profound changes in physical properties [8]. Moreover, many materials show reactivity in water, such as the hydrolysis reaction. Thereby, the reactive species can cause inhomogeneous chemical composition of the final material [9]. For this reason, using water as a medium is not appropriate in many cases. Thus, there is an increasing need to develop ceramics by the dispersion of particles in non-aqueous media.

DMF is an excellent polar inert organic solvent which has wide and important industrial and academic significance [10,11]. It has a good dissolving capacity and chemical stability to many organic and inorganic compounds, even named as a "versatile organic solvent". Of particular interest here is the unique properties exhibited by DMF, which can open new opportunities in the field of functional ceramics preparation. DMF contains no active hydrogen, so chain transfer reaction of radical polymerization takes place less readily. In addition, the surface tension of DMF is 36.2 mN/m at 25 °C, which is almost one-half of that of the water (71.81 mN/m). Thus it will cause limited shrinkage during green-body drying when used as a vehicle of ceramics slurry [12]. To the best of our knowledge, there is scarcely published report available on the dispersion stability of particles in DMF.

A well-dispersed alumina–DMF suspension can be of interest for the manufacture of high performance ceramics. In non-water solvent, the dispersant molecular structure has great influence on the dispersion of powder particles. It is reported that –COOH group as an anchoring group can bind effectively with the powder surface [13]. Citric acid contains three –COOH groups in its molecular structure, and is the most extensively investigated dispersant for ceramic suspension in aqueous solution [14,15]. Herein, we investigate the interaction and dispersion stability of alumina suspension with citric acid in DMF. It is found that the adsorption amount of citric acid depends on the pH$_a$ values, and the maximum adsorption appears at pH$_a$ 2.6. The interaction of citric acid with alumina was characterized by monitoring the evolution of UV–vis spectra, zeta potential values, and FT-IR spectra. This study may serve as a reference model for other kinds of liquid dispersions of this kind.

2. Experimental

2.1. Materials

An as-received alpha-alumina powder (Almatis, CT 3000 SG, Qingdao, China, d$_{50}$ = 0.8 μm, surface area = 7.5 m^2/g) was employed.

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It was dried in an oven at 100 °C for 24 h before use. All the chemicals were of analytical grade and used as-received. If there is no specific explanation, the citric acid dosage in this paper is given as the weight concentration of the pure citric acid relative to alumina.

2.2. Instrumentation and measurements

The zeta potential of very dilute DMF alumina suspension (0.01 vol.%) was measured on a Malvern instruments model Zetasizer Nano-Z (Malvern, UK). After the suspension was stirred thoroughly and ultrasonicated for 15 min, 5 mL of the suspension was transferred into a measuring cell. The pH_a was adjusted in the range of 2 to 12 using HCl (0.5 M) and NaOH (0.5 M), which was done automatically by the instrument. The tests were repeated three times in order to obtain accurate results.

Adsorption of citric acid onto alumina was conducted using depletion method and UV–vis spectroscopy measurement. 5 wt.% alumina suspension samples containing varying citric acid concentration were firstly ultrasonicated for 30 min, and set 24 h in order for the equilibrium to be reached, and finally centrifuged for 20 min at 12,000 rpm. Then, an aliquot of the supernatant was carefully collected and analyzed for the dispersant concentration. Citric acid can react with orange–red ferric 5-nitrosalicylate solution and reduce the Fe^{3+} species to Fe^{2+} species, thereby decreasing the absorption of the solvent in a wide range of wavelengths [16,17]. This phenomenon was used as the basis to determine the amount of citric acid. For this purpose, 2 mL of 7.0×10^{-4} M ferric 5-nitrosalicylate solutions were placed into a series of 4 mL volumetric flasks. Then, the above supernatant solutions were mixed with the ferric 5-nitrosalicylate solutions and examined with a calibrated Shimadzu UV-2550 spectrophotometer (Kyoto, Japan) at room temperature. The calibration curve for citric acid was obtained following similar procedure. The adsorbed amount was calculated by detracting the citric acid left in the supernatant from the total amount.

FT-IR spectra of the particles interacting with citric acid were recorded on a Nicolet-Nexus model 670 Fourier transform infrared spectrophotometer (Wisconsin, USA) by accumulating 64 scans. Before being analyzed, the alumina powder interacted with citric acid was gently washed with DMF solvent at the experimental pH_a values in order to remove any non-adsorbed citric acid. Then, the samples were dried in a vacuum oven at less than 5×10^{-3} Torr without exceeding temperature of 25 °C for 30 h.

3. Results and discussion

3.1. Zeta potential

DMF is a kind of polar and high permittivity solvent, whose pH_a values can be effectively regulated by HCl [18]. This provides valuable reference for us to regulate the system pH_a values. The zeta potential of DMF-based alumina suspension is shown in Fig. 1. The isoelectric point of the bare alumina particles occurs at about pH_a 7.6. However, when 2 wt.% citric acid was added into the system, the pH_{IEP} of alumina particles is shifted from approximately pH_a 7.6 to 5.2 for the negative charge carriers nature of citric acid changes the surface property of the particles. The specific energy of the interaction between alumina particles and citric acid can be calculated using the following equation [19],

$$\Delta pH_{IEP} = 1.0396 C_0 \exp\left(\frac{-\Delta G_{SP}^0}{RT}\right) \tag{1}$$

where ΔpH_{IEP} is the shift of the isoelectric point; C_0 is the additive concentration of the dispersant and $(-\Delta G_{SP}^0)$ represents the corresponding specific free energy on interaction between alumina
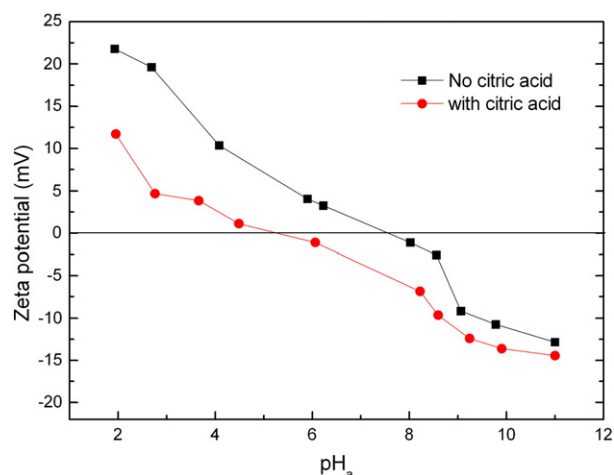

Fig. 1. Zeta potential of alumina particles with and without citric acid as a function of pH_a in the DMF solvent.

and citric acid. R and T are the standard gas constant and the absolute temperature in K, respectively. Table 1 shows the computed data of the interaction energy. From these computations, $(-\Delta G_{SP}^0)$ appears around $-7.2RT$ unit, indicating that citric acid can be adsorbed onto the surface of the alumina particles.

3.2. UV–vis spectroscopy measurement

Fig. 2 plots the adsorption curve of citric acid as a function of the suspension pH_a values. The concentration of citric acid is 800 ppm. It can be seen that the adsorbed amount highly depends on the pH_a values, and the highest adsorbed amount is at pH_a 2.6. Here in contrast to an aqueous solution, the citric acid dissolved in DMF solvent shows a hypsochromic shift of the highest adsorption amount from about pH 5.5 [20] to pH_a 2.6. This phenomenon may relate to the nitrogen and oxygen atoms existing in DMF solvent forming hydrogen bonds with the carboxyl groups of citric acid, thereby promoting its dissociation.

The adsorption isotherms for citric acid on alumina at pH_a 2.6 and 10.9 are presented in Fig. 3, which are plots of the adsorbed amount per unit area Γ (mol/m²) as a function of the equilibrium (residual) concentration in solution C_{eq} (mol/L). From this figure it appears that the adsorbed amount rises with an increase of the citric acid concentration. The adsorbed amount at pH_a 2.6 was higher than that at pH_a 10.9. To determine whether monolayer adsorption occurs for the DMF-based alumina suspension, the data have been analyzed by employing the Langmuir monolayer adsorption equation [21]:

$$\frac{C_{eq}}{\Gamma} = \frac{C_{eq}}{\Gamma_{max}} + \frac{1}{K\Gamma} \tag{2}$$

where Γ_{max} (mol/m²) is the adsorbed amount per unit area at saturation (on the plateau of the isotherm); K is a constant; C_{eq} (mol/L) is the equilibrium concentration of adsorbate in solution; Γ (mol/m²) is the adsorbed amount for a given equilibrium concentration. The data of Fig. 3 replotted in Fig. 4 were linear in the whole experimental concentration regime, indicating that in the DMF-based suspension the adsorption of citric acid followed the Langmuir equation. The values of

Table 1
Computed value of specific free energy of interaction for alumina and citric acid.

System	Concentration (ppm)	pH_{IEP}	ΔpH_{IEP}	$-\Delta G_{SP}^0$ (RT units)
Without citric acid	–	7.6	–	–
With citric acid	3000	5.2	2.4	7.2
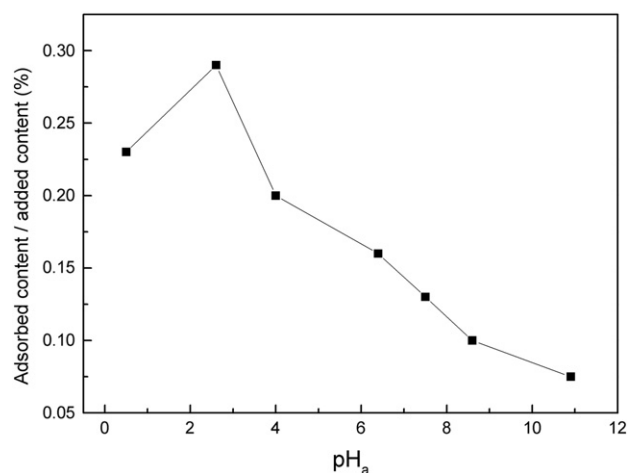
Fig. 2. Adsorption behavior of citric acid on alumina surface as a function of pH_a.

Fig. 4. Replot of Fig. 3 based on the Langmuir equation.

Γ_{max} derived from a linear regression to the data are given in Table 2. The values of Γ_{max} are in good agreement with the plateau adsorption inferred from Fig. 3, which further make it plausible that the citric acid molecules are adsorbed on the surface of alumina in DMF solvent as a monolayer.

3.3. FT-IR measurement

Fig. 5 shows the FT-IR spectra of alumina and citric acid-treated alumina at pH_a 2.6 and 10.9. The purpose of this study was to analyze the interaction between the components of the suspension. Citric acid binds with alumina powders through the interaction of –COOH group of citric acid with –OH group located on the powders [20]. For this reason the analysis was limited in the range of 1000–2000 cm^{-1} wavenumber. There are two absorption bands in the spectrum of a pure alumina powder (Fig. 5a). The band at 1402 cm^{-1} corresponds to –OH deformation vibration on the alumina surface. The band at 1576 cm^{-1} is due to the presence of moisture in the sample [22]. Fig. 5b exhibits the spectrum of alumina modified on its surface with citric acid at pH_a 2.6. The band at 1394 cm^{-1} corresponds to –OH vibration, whereas the band at 1655 cm^{-1} corresponds to the asymmetric C=O stretching vibration. However, the band of 1576 cm^{-1} for the presence of moisture cannot be found. This indicates that the water molecules are exchanged almost completely by the citric acid. In the spectrum of citric acid-treated alumina at pH_a 10.9, both the characteristics of the pure
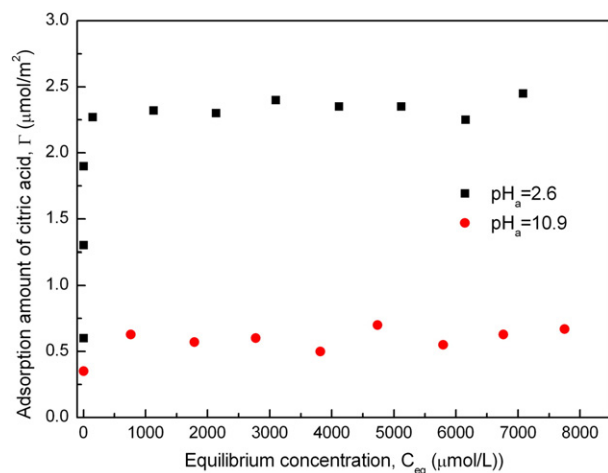
Table 2
The saturation coverage determined by fitting the adsorption data in Langmuir equation.

pH_a	Γ_{max} ($\mu mol/m^2$)
2.6	2.3
10.9	0.7

alumina and alumina treated with citric acid at pH_a 2.6 can be detected. There is a band at 1398 cm^{-1} corresponding to –OH deformation vibration, a band at 1653 cm^{-1} corresponding to the C=O asymmetric stretching vibration, and a band at 1593 cm^{-1} due to the presence of water molecules in surface of the alumina powder. This indicates that there are still some water molecules not being exchanged by the citric acid and the surface of alumina has been partly covered by the citric acid molecules at pH_a 10.9.

3.4. Sedimentation experiment

The stability of DMF-based alumina suspension with citric acid was examined by sedimentation test. Fig. 6 shows the dispersion behavior of a 5 wt.% alumina suspension with citric acid. Compared to the DMF-based alumina suspension without citric acid (Fig. 7), the addition of citric acid can improve the stability of the suspension. It can be found that the stability of DMF-based alumina suspension with

Fig. 3. Adsorption isotherms, the amount of citric acid adsorbed in alumina suspension as a function of equilibrium concentration at pH_a 2.6 and 10.9.
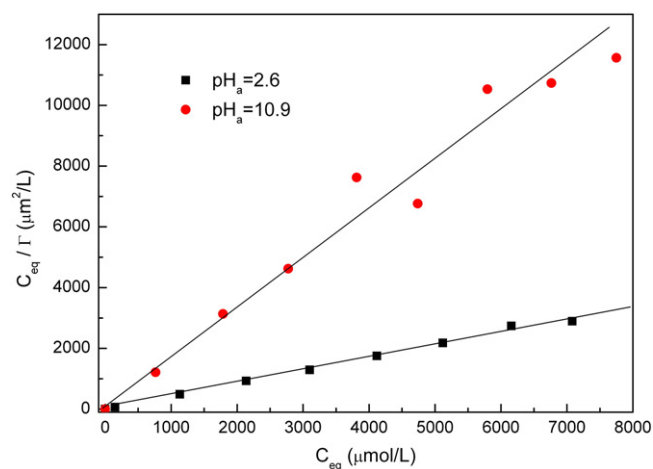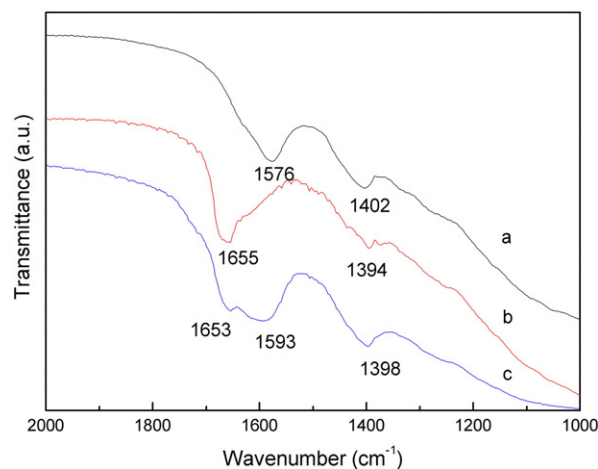

Fig. 5. FT-IR spectra of alumina powder from suspensions prepared at different pH_a values: (a) without citric acid, (b) citric acid-treated alumina at pH_a 2.6, (c) citric acid-treated alumina at pH_a 10.9.

Fig. 6. Photograph of sedimentation measurement for DMF-based alumina suspension with citric acid at different pH_a values. From right to left, $pH_a = 0.5, 2.6, 4.0, 6.4, 7.5, 8.6, 10.9$. A) 1 min; B) 72 h.

citric acid depends on the pH_a values. When the pH_a values were higher than 4, the alumina particles had poor dispersion stability and flocculation had occurred after 72 h sedimentation. When the pH_a values were below 4, the stability of the suspension in the solvent increased. The highest stability of the suspension took place at pH_a 2.6.

3.5. Discussion on dispersion stability of DMF-based alumina suspension

The stability of suspension depends on the sign and the magnitude of total interparticle potential energy, V_T [23]. The general equation for describing V_T concerns the sum of the repulsive and attractive contributions,

$$V_T = V_A + V_R \tag{3}$$

where V_A is the attractive potential energy due to long range van der Waal's forces, and V_R encompasses electrostatic, steric, and other repulsive potential energies. The stability of the dispersion can be achieved when the repulsive forces are high enough to overcome the attractive van der Waal's forces [24]. Electrostatic repulsion results from the development of an electrical double-layer around each particle when the particles are dispersed into a polar liquid, which depends on the dielectric constant of the medium. The dielectric constant of water is 78.5 F/m, whereas the dielectric constant of DMF is 36.7 F/m. Citric acid can be effective in aqueous alumina suspensions based on the function of electrostatic repulsion [25]. However, it is less effectively to stabilize
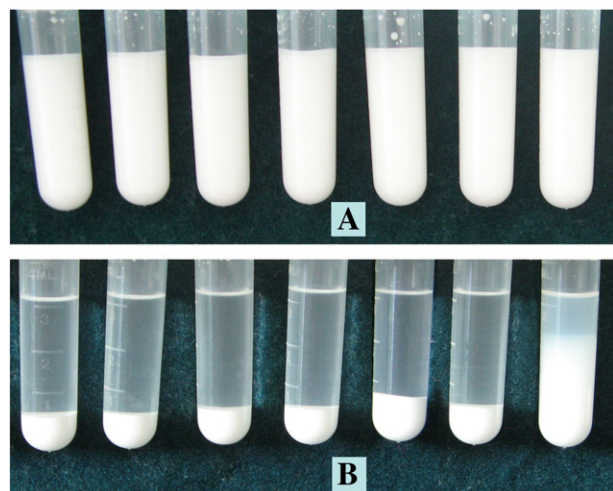

Fig. 7. Photograph of sedimentation measurement for DMF-based alumina suspension without citric acid at different pH_a values. From right to left, $pH_a = 0.5, 2.6, 4.0, 6.4, 7.5, 8.6, 10.9$. A) 1 min; B) 72 h.

ceramic particles in the majority of non-aqueous media than in water because of the lower dielectric constant for non-aqueous media. Boger et al. have found that small molecules can be effective in stabilizing dispersion in organic media by modifying the Hamaker constant of the particles, which leads to the decrease of the van der Waal's attraction between particles [26]. Graule et al. have found that the tail of dispersants being well dissolved in the non-aqueous organic solvents can also reduce the Hamaker constants of particles and may give rise to sterical stabilization, which makes suspension keep a high stability [13]. It should be noted that any group on the citric acid molecules, –OH, –COOH and –CH$_2$–, has a good solubility in DMF. The more citric acid molecules are adsorbed, the better to modify the Hamaker constant of the particles and to enhance the steric hindrance. The suspension stability is decided by the sum of van der Waal's forces, electrostatic and steric repulsions. The function of steric and electrostatic stabilization is raised because the relatively more adsorption of citric acid greatly decreases the attractive van der Waal's forces between particles at low pH_a values. As a result, the repulsive potential energy is higher than the attractive potential energy. So, when the pH_a is selected at a value below 4, the DMF-based alumina suspensions have a high dispersion stability. The highest stability occurs at pH_a 2.6 where the maximum absorption amount happened. When the pH_a values are higher than 4, the adsorbed amount diminishes with increasing pH_a values. The value of Γ_{max} reduces from 2.3 μmol/m^2 at the pH_a value of 2.6 to 0.7 μmol/m^2 at the pH_a value of 10.9. Less citric acid molecules adsorbed on the alumina particles will result in the Hamaker constant of the particles keeping at a high value and the steric repulsion being almost neglected. Although the zeta potentials of alumina particles with citric acid in DMF solution in pH_a range of 8–11 are higher than that at pH_a 2.6, the electrostatic and steric repulsions cannot overcome the attractive van der Waal's forces and thus the alumina particles exhibit poor dispersion stability. Furthermore, at high pH_a values, more non-adsorbed citric acid molecules left in solvent may act as a flocculant for the bridging or depletion effects. This may also make the alumina suspension have a poor stability. This explanation is in accordance with the experimental phenomena. However, to understand the real mechanism of DMF-based alumina suspension with citric acid as dispersant, the further detailed analysis and theoretical study are necessary.

4. Conclusions

The dispersion stability of alumina suspensions in DMF solvent has been investigated in the presence of citric acid. The adsorption of citric acid follows the Langmuir type and the adsorption density in pH_a 2.6 is almost three times as great as that in pH_a 10.9. The IEP of the alumina suspension can be shifted from approximately pH_a 7.6 to 5.2 with 2 wt.% of the citric acid concentration. The specific interaction energy between the alumina and citric acid is $-7.2RT$ unit. The sedimentation test exhibits that the adsorption amount on the surface of alumina plays a key role in the suspension stability. A suitable case for using citric acid as dispersant for DMF-based alumina suspension is at pH_a below 4, and the best condition is pH_a 2.6.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.powtec.2010.06.009.

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