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Interaction and dispersion stability of alumina suspension with PAA in N,N′-dimethylformamide

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Abstract

The alumina suspension in N,N′-dimethylformamide (DMF) was studied in the presence of a polyacrylic acid (PAA) dispersant. The sedimentation measurements of the suspensions show that PAA can impart favorable dispersion stability to alumina in DMF over a wide apparent pH (pH_a) range. The adsorption of PAA on alumina and the zeta potential of the suspension are pH_a dependent. FTIR-ATR spectroscopic studies reveal that the different interaction mechanisms between PAA and alumina work as a function of pH_a. But the observable difference of dispersion between pH_a values of 2.6–12.7 is small according to the sedimentation experiments. This can be explained by a combination of the static effect of PAA dispersant and different sizes of steric barrier resulting from the configurational variation of PAA with changing pH_a values.

Keywords: Suspensions; Al_2O_3; Polyelectrolyte; Interfaces; Functional applications

1. Introduction

The excellent properties of alumina, such as chemical and thermal stability, high strength, wear resistance, make it attractive for many types of engineering applications. Electronics, structural and functional ceramics, and biomedical implantation could all benefit from these attractive properties.[1,2] A well-dispersed and stable alumina slurry is essential to the ceramic industry processes such as slip-casting, tape-casting, injection molding, direct coagulation casting and gel-casting.[3–6] The stabilization of alumina in aqueous solution has been extensively studied.[7–11] However, there are a few drawbacks of using water for preparation of high performance ceramics, especially for some functional materials, such as porous ceramics. The high surface tension of water directly brings on a large capillary force in the solvent removing process, resulting in considerable and irreversible shrinkage which is accompanied by profound and unwanted changes in physical properties.[12] To prevent cracking and fracture of the components that can be induced by solvent evaporation, the drying stage needs to be handled extremely carefully and slowly at room temperature under conditions of appropriate humidity,[13] and over an extended period of time. So the drying step is thought to be a time-consuming and tedious process.[14] Moreover, many materials show reactivity in water, such as hydrolysis reaction. The reactive species can cause inhomogeneous chemical composition of the final material.[15] Therefore using water as a solvent is not appropriate in many cases. Thus, it is highly desirable to develop and explore ceramic particles dispersion and functional ceramics preparation in a non-aqueous solvent system.

DMF is an excellent polar organic solvent. It is miscible with water, alcohol, ether, chloroform and many other organic solvents. Moreover, it has a good dissolving capacity and chemical stability to many organic and inorganic compounds. Despite some toxicity compared with green solvent water, DMF's usefulness as a "versatile organic solvent" still finds wide and important industrial and academic significance.[16,17] Of particular interest here are the unique properties exhibited by DMF, which can open new opportunities in the field of functional ceramics preparation. The excellent solvent power of DMF can easily dissolve the monomers used in gel-casting technology. At the same time, DMF contains no active hydrogen, so the chain transfer reaction is reduced. In addition, the surface tension of DMF is 36.2 mN/m at 25 °C, almost one-half that of

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water (71.81 mN/m). Thus it will cause limited shrinkage during green-body drying when used as solvent for a ceramics slurry. We have used this kind of solvent to successfully prepare well porous alumina ceramic without harsh drying limitations. Relevant work is in production. Nevertheless, to our knowledge, there are no studies on particle dispersion stability in DMF.

PAA, as one kind of anionic polyelectrolyte dispersant, has an attractive feature of conferring stability both by electrostatic and steric forces and finds wide-spread practical applications as a stabilizer or a flocculent in many technological processes.[18,19] In this study, we choose PAA as dispersant and the effect of PAA on DMF-based alumina suspensions was analyzed and discussed using data obtained from different methods. The adsorption of PAA on alumina and the zeta potential of the particles are reported as a function of pH_a values. The interaction between alumina and PAA is discussed based on the use of FTIR-ATR spectroscopy. Finally, the stability mechanism of PAA on the DMF-based alumina suspension is proposed according to experimental results and physicochemical properties of alumina and PAA. Our detailed studies on the effect of PAA to alumina suspension in DMF not only provide a better control of suspension stability which would extend the potential for the production of high performance ceramics but also give an insight into the function and reaction of dispersants in organic solvents.

2. Experimental procedures

2.1. Materials

An as-received alpha-alumina powder (Almatis, CT 3000 SG, China, $d_{50} = 0.8\ \mu m$, surface area = $7.5\ m^2/g$) was employed. All the chemicals were of analytical grade and used as-received. DMF served as the solvent for all samples and was purchased from Shanghai Chemical Reagent Company, China. $NH_3 \cdot H_2O$, NaOH and HCl were used for pH_a adjustment. A commercially available dispersant PAA (Taihe Water-Treatment Co. Ltd., China) was provided as 50 wt% solution. The producer claims it has an average molecular weight of 5000 Da, and its counter ion is H^+. If there is no specific illustration, the PAA dosage in this research is given as the weight concentration of the pure PAA relative to alumina.

2.2. Instrumentation and measurements

The measurement of the dispersion characteristics of the DMF-based alumina suspensions was carried out using sedimentation experiments. HCl and $NH_3 \cdot H_2O$ solutions were employed as the acid-base regulator. The measurement of pH_a values was according to IUPAC standard,[20] given by a PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). 0.05 mol/kg potassium hydrogen phthalate was used as the pH reference material. The adjusted DMF solvent was divided into two groups. One had 1 wt% PAA added, and the other without any dispersant. All experiments were conducted in the 20 wt% alumina solution. The mixtures of all samples were ultrasonicated for 30 min, and then were stood without any disturbance for 72 h.

The adsorption of PAA onto alumina particles was conducted using the depletion technique and UV/vis spectroscopy. The 20 wt% alumina suspension was flocculated with 3000 ppm PAA in DMF solvent. The suspension was then ultrasonicated for 30 min, and set 24 h in order for equilibrium to be reached, and finally centrifuged for 20 min at 12,000 rpm. An aliquot of supernatant was carefully collected and analyzed for the dispersant concentration. The concentration of PAA in solution was determined using a colorometric technique by UV/vis spectrophotometry (UV-2550, Shimadzu, Japan). Polyacrylic acid complexation involved the interaction of carboxylate group with a Bio-Rad Protein Assay dye (Bio-Rad Chemical Division, USA). When PAA was added into the Bio-Rad dye solution, the absorbance at 585 nm increased linearly with the increasing polymer concentration.[21,22] This phenomenon was used as the basis to determine the amount of PAA. The adsorbed amount was calculated by detracting the PAA left in the supernatant from the total amount.

The zeta potential of very dilute DMF-based alumina suspension (0.01 vol% solid loading) was measured at 25 °C on a Zetasizer Nano Z (Malvern instrument, UK). After the suspensions were thoroughly stirred and ultrasonicated for 15 min, 5 ml of the suspension was transferred into a measuring cell. The pH_a was adjusted by means of instrument automatic titration in the range of 2–12 using HCl (0.5 M) and NaOH (0.5 M). The tests were repeated three times in order to obtain accurate results.

FTIR-ATR spectra were carried out by using a Nicolet-Nexus 670 Fourier transform infrared spectrometer. The specimens were prepared by pressing spectroscopic grade KBr powder (1.320 ± 0.04 g) mixed with 2 wt% powdered sample into a pellet. The spectrum of bare alumina was subtracted from that of the polymer adsorbed particles to give the spectra of PAA that interacted with the particles. Before being analyzed, the alumina particles that interacted with the polymer were gently washed with DMF solvent at the experimental pH_a values in order to remove any non-adsorbed PAA. Then, the samples were dried in a vacuum oven (less than 5×10^{-3} Torr) without exceeding 25 °C for 30 h.

3. Results and discussion

3.1. Sedimentation experiment

DMF is a type of polar and high permittivity solvent, whose pH_a values can be effectively regulated by HCl.[23,24] This provides a valuable reference for us to regulate the system pH_a values. The sedimentation experiment was divided into two groups: one with PAA as dispersant and the other with bare alumina solution as a contrast test. It was found that in the pH_a range from 2.6 to 12.7, bare alumina had a poor dispersion stability and flocculation formed after 72 h placement. The dispersion stability was remarkably improved with 1 wt% PAA dispersant (as shown in Fig. S1). PAA provides a favorable dispersion function in a wide pH_a range, extending from 2.6 to 12.7. There is slightly better dispersion at pH_a 2.6 and 4.0. It is speculated that this is due to the difference in adsorption characteristics in different pH_a values. The explanation could be argued so we carried

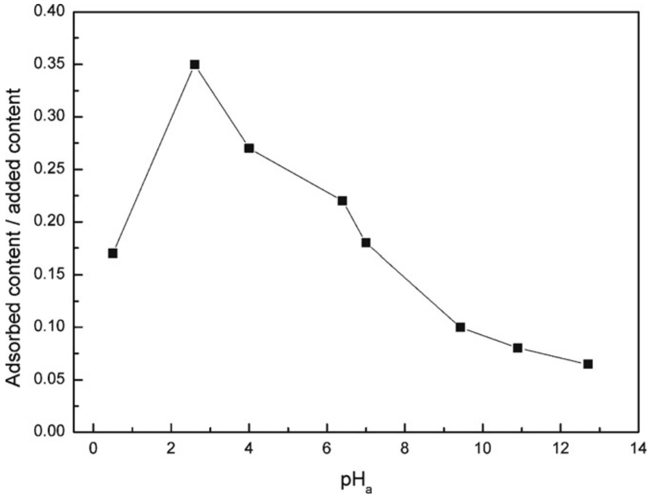

Fig. 1. Adsorption curve of PAA on alumina surface as a function of pH_a.

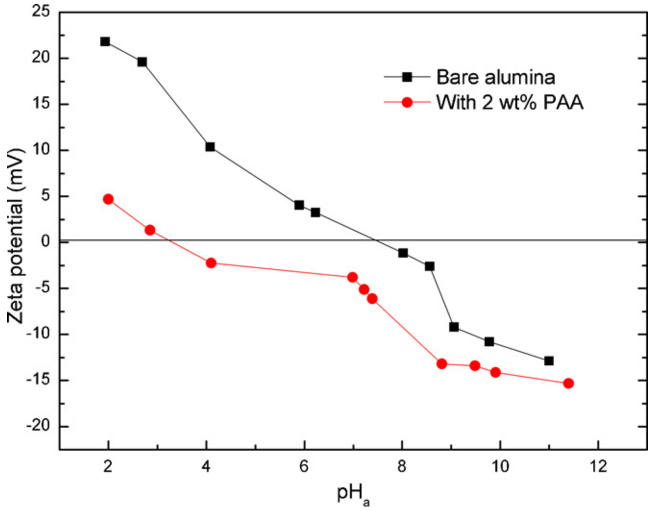

Fig. 2. Influence of pH_a on the zeta potential of alumina particles in the absence and presence of PAA.

out further adsorption experiments using UV/vis spectroscopy testing. From the sedimentation experiment, we observed that the alumina suspension with PAA as the dispersant had a more inferior dispersion stability than the bare alumina suspension in pH_a 0.5. The reason for this result may be that this pH_a value is far below the pK_a of the PAA (around pH 4.5). At such a strong acid condition, PAA is fully protonated, and the bare alumina is also strongly protonated. As a result, PAA acts as a flocculant for the bridging or depletion effects caused by the non-adsorbed PAA molecules.

3.2. *PAA adsorption measurements*

Fig. 1 plots the adsorption curve of PAA as a function of pH_a values. A sharp increase of the adsorbed amount between pH_a 0.5 and 2.6 is observed. The adsorbed amount then diminishes with increasing pH_a values. The pH_a dependence found here is similar to the previously reported data for the adsorption of acrylate polymers on alumina in aqueous[25] and ethanol solutions.[26] The adsorption of PAA onto alumina is influenced by the pH_a values because both the particles surface charges and the electrolyte dissociation are pH_a dependent. In contrast to the aqueous solution, the PAA dispersed in DMF solvent shows a hypsochromic shift of the highest adsorption amount from about pH 4.5[25] to pH_a 2.6. It may be the reason that the nitrogen and oxygen atoms existing in DMF solvent can form hydrogen bonding with carboxyl groups of PAA polymer, thus promoting the dissociation of PAA. Furthermore, the hydrophile–lipophile balance (HLB) value of the PAA is strongly influenced by the change of the solvent from water to DMF.[27] Both of the functions of hydrogen bonding and HLB value change may lead to the shift of the highest adsorption peak.

3.3. *Zeta potentials of alumina in DMF solvent*

The zeta potential of particles in aqueous suspension plays an important role in overcoming the interparticles Van der Waals force and keeping the system stable. But for most organic solvents, the dissociation and the solvent ionization capability are often extremely low. It is usually considered that the surface charge offers limited protection in prohibiting flocculation in non-aqueous solvent. While DMF bears relatively high permittivity, and previous research work has clearly exhibited that the dispersion stability in a non-aqueous solution, especially for polar hydrocarbon solvents, can be achieved by the electrostatic effect.[28] Therefore, the electric double layer repulsion in a DMF system should not be neglected. The zeta potential of alumina particles with and without PAA dispersant in DMF solution was evaluated in the pH_a range of 2–12. The results presented in Fig. 2 reveal that the zeta potentials of alumina suspensions are varied as a function of pH_a values. The isoelectric point (IEP) of the bare alumina suspension occurs at pH_a 7.6, which is slightly lower than the reported bare alumina IEP pH 8.1 tested in an aqueous solution.[29] It could be the reason that DMF molecules can form hydrogen bonding with the surface of the particles, as shown in Fig. S2. This interaction results in a shift of the bare alumina IEP to a lower pH_a value due to the alkaline nature of DMF. The addition of PAA dispersant is able to effectively shift the IEP to about pH_a 3.2. It is because the dispersant PAA used here is a kind of anionic polyelectrolyte with an average molecular weight of 5000 Da and which bears many dissociable protons. Once deprotonated, these molecules can play as “negative charge carriers” to change the electrokinetic properties of alumina particles. This leads to charge inversion from positive to negative, thus making a variation of the IEP to lower pH_a values.

The specific energy of interaction between the alumina powder surface and dispersant PAA could be calculated using the following equation[30]:

$$\Delta \mathrm{pH}_{\mathrm{IEP}} = 1.0396 C_0 \exp\left(\frac{-\Delta G^0_{\mathrm{sp}}}{RT}\right) \tag{1}$$

where $\Delta \mathrm{pH}_{\mathrm{IEP}}$ is the shift in the isoelectric point at the dispersant concentration C_0. ΔG^0_{sp} represents the corresponding specific free energy of interaction between the alumina powder surface

Table 1
The major infrared species vibrations summarized for PAA, PAA sodium salt and their adsorption onto alumina particles at various pH_a values.

	C=O (cm^{-1})	$\upsilon_{asym}COO^-$ (cm^{-1})	$\upsilon_{sym}COO^-$ (cm^{-1})	Separation, $\Delta\upsilon$ (cm^{-1})
PAA	1721			
PAA sodium salt		1591	1408	183
pH_a 0.5	1701	1631	1406	225
pH_a 2.6	1713	1617	1405	212
pH_a 4.0		1579	1408	171
pH_a 9.4		1569	1410	159
pH_a 12.7		1545	1408	137

and PAA molecules. R and T are the standard gas constant and the temperature (K), respectively. The calculated interaction energy value for PAA adsorbed on alumina surface is −12.79 (*RT* units) by using the data presented in Fig. 2. This indicates that PAA can be adsorbed onto the surface of alumina through chemical interaction, hydrogen bonding or electrostatic interaction. To further characterize the mechanism of adsorption of PAA on alumina, FTIR-ATR spectroscopy was employed, which provides specific information on the surface of the particles.

3.4. *FTIR-ATR spectroscopy*

FTIR-ATR can be used to identify the mechanism of surfactant adsorption onto the oxide particles. The FTIR-ATR results obtained for the PAA, PAA sodium salt and PAA adsorbed onto alumina particles at various pH_a values are shown in Fig. 3 and summarized in Table 1. There is a C=O stretching band appearing in the range of 1701–1721 cm^{-1}, a COO^- antisymmetric stretching band in the range of 1545–1631 cm^{-1}, a COO^- symmetric stretching band at ∼1405 cm^{-1}, a CH_2 antisymmetric stretching band at ∼1458 cm^{-1}, and a C–C–C antisymmetric stretching band at ∼1152 cm^{-1}. Obviously, the C=O and COO^- stretching vibrations of the interfacial dispersant are different with the separation measured for the corresponding sodium salt. Graule and Gauckler[31] have pointed out that this difference is ascribed to the formation of an innersphere complex between the dispersant and the alumina surface.

By comparing the separation of the symmetric and antisymmetric stretching frequencies ($\Delta\upsilon = \upsilon_{asym} - \upsilon_{sym}$) of the carboxylate ion adsorbed on the surface of oxide surfaces with the separation measured for the corresponding sodium salt, we were able to identify the bonding mechanism.[32–35] When there is a distinct C=O character in the spectrum, and $\Delta\upsilon_{adsorbed}$ is bigger than $\Delta\upsilon_{salt}$, the monodentate structure takes place. When there is no C=O character in the spectrum and $\Delta\upsilon_{adsorbed}$ is smaller than $\Delta\upsilon_{salt}$, the adsorption mechanism is bidentate chelating. When there is no C=O character in the spectrum and $\Delta\upsilon_{adsorbed}$ is similar to $\Delta\upsilon_{salt}$, the adsorption structure is bidentate bridging.

When PAA adsorbed at pH_a 0.5, $\Delta\upsilon_{adsorbed}$ (225 cm^{-1}) is far bigger than $\Delta\upsilon_{salt}$ (183 cm^{-1}) and the C=O stretching band at 1701 cm^{-1} can be found. These features indicate that the monodentate chelation is the mode of chemisorption. Furthermore, we can see that the C=O stretching band exhibits a downward frequency shift compared to that of PAA molecules. This

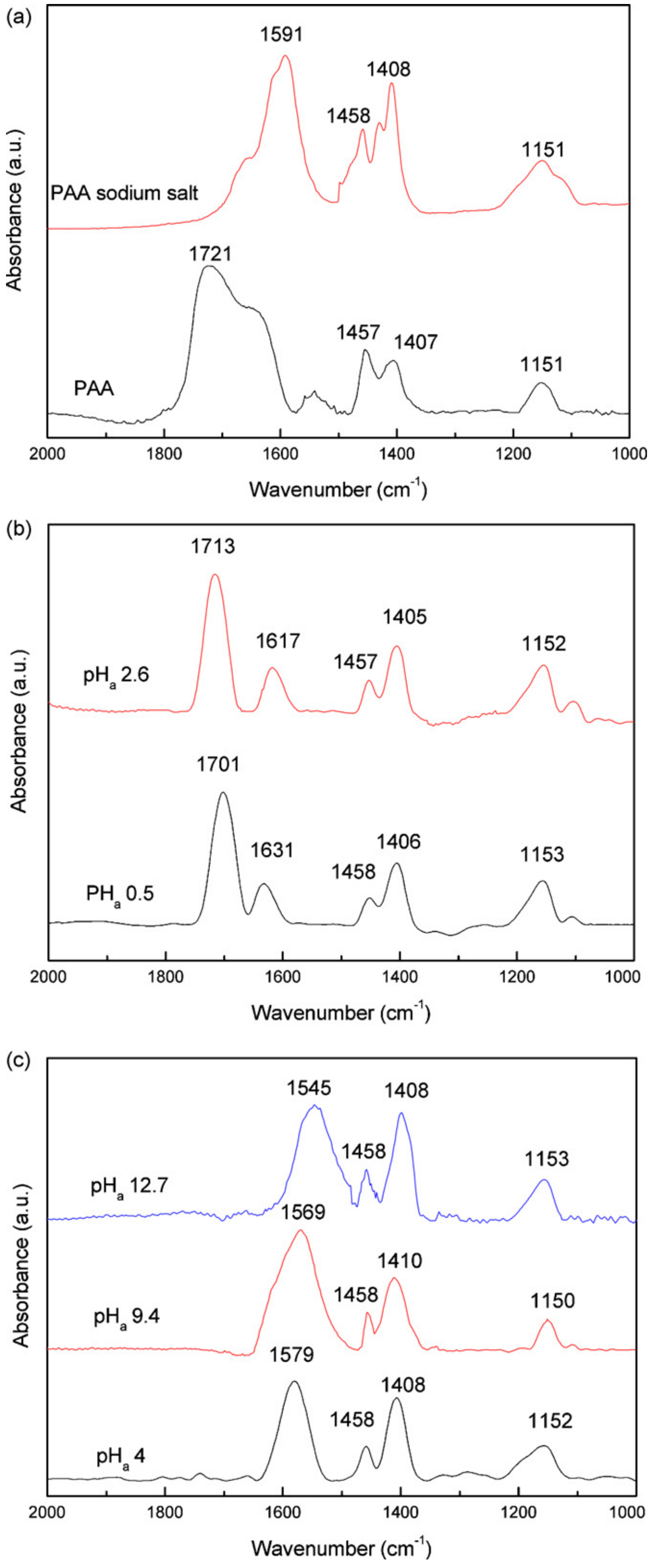

Fig. 3. FTIR-ATR spectra of (a) PAA and PAA sodium salt, (b) PAA adsorbed onto alumina at pH_a 0.5 and 2.6, and (c) PAA adsorbed onto alumina at pH_a 4, 9.4, 12.7.

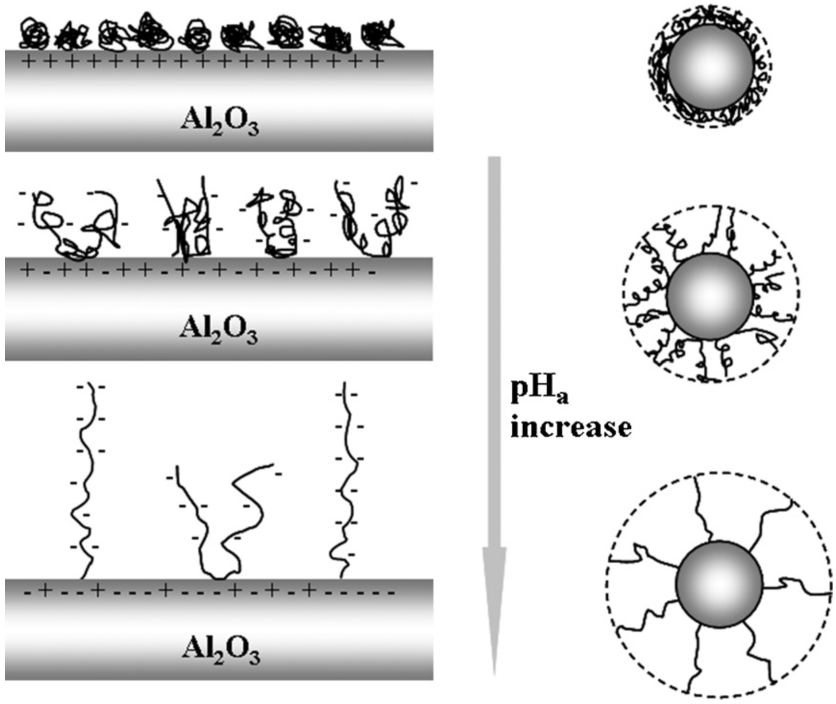

Fig. 4. The illustration of proposed variation in PAA polymer conformation at changing pH_a conditions.

decrease in wavenumber after adsorption is indicative of hydrogen bonding.[36] This characteristic suggests that a monodentate structure with hydrogen bonding has occurred. The FTIR-ATR spectrum of PAA adsorbed at pH_a 2.6 shows a similar phenomenon, which has the C=O stretching band at 1713 cm^{-1} as well as exhibiting a downward frequency shift compared to that of PAA molecules. The value of $\Delta\upsilon_{adsorbed}$ (212 cm^{-1}) is greater than that of $\Delta\upsilon_{salt}$ (183 cm^{-1}). These results indicate that monodentate structure and hydrogen-bonded structure occur when $pH_a \leq 2.6$.

In the case of PAA adsorption at pH_a 4.0, the monodentate and hydrogen-bonding characteristics are reduced substantially with the ~1721 cm^{-1} band almost disappearing. The separation, $\Delta\upsilon_{adsorbed}$, is reduced to 171 cm^{-1}, and is smaller than that of the PAA sodium salt (183 cm^{-1}). This suggests that bidentate chelation is the mode of chemisorption. Similarly, when PAA is adsorbed at pH_a 9.4 and 12.7, the values of $\Delta\upsilon_{adsorbed}$ are 159 and 137 cm^{-1}, respectively. These results indicate that bidentate chelation is the main adsorption mechanism when $pH_a \geq 4$.

3.5. Discussion on dispersion stability mechanism

The dispersion performance had been expected to vary greatly with changing pH_a values, for PAA is a polyelectrolyte and its degrees of dissociation and adsorption on alumina in DMF have been proven to be substantially affected by pH_a values. While it was unexpected according to the sedimentation phenomena (shown in Fig. S1), their dispersion difference was hard to perceive in a wide pH_a range in spite of the different adsorption amounts, zeta potential and interaction mechanisms given by experimental tests. Analyzing this, we found two possible explanations that may be responsible. Firstly, in the case of pH_a values below seven, the absolute value of zeta potential (shown in Fig. 2) is very low. Therefore the force of electrostatic repulsion is too poor to overcome the attraction force between the particles. Notwithstanding the high adsorption density in this range (shown in Fig. 1) the steric effect may be the main or the sole resource to prevent flocculation. Similar viewpoints of stabilization were also found by de Hazan et al.[11] for the adsorption of comb polyelectrolytes onto colloidal alumina particles in DI water. With increasing pH_a, electrostatic repulsion made the PAA adsorption difficult, while the same electrical characteristic between particles and dispersant leading to even a slight amount of adsorption obviously augmented the zeta potential. Thus, a combination of static and steric effects, called electrosteric stabilization, jointly stabilizes the suspension. So, a decrease in the adsorption could still make the particles disperse well. This analysis shows that the dispersion behavior of alumina in DMF is affected by electrostatic and steric repulsion forces and this is basically in agreement with the classical DLVO theory.

Secondly, this can be explained by the difference in the conformation of PAA adsorbed onto alumina. A hypothesis schematic representation is presented in Fig. 4. The dissociation degree of PAA molecules in solvent depends on pH.[37,38] In a low pH_a range, they form a tightly bound coil in solution, whereas increasing the pH_a causes the functional groups to dissociate and repel one another. Such that the coil partly unwinds, until in a high range of pH_a, the groups are fully dissociated. Highly charged linear polyelectrolyte is known to acquire a stretched conformation at the surface of particles. Increasing the pH_a values enlarges the distance of particles and may remedy the decrease in the adsorption amount. These two explanations are not in conflict, and both are in accordance with the experimental phenomena. However, which one plays the main role may need further detailed study.

4. Conclusion

PAA imparts favorable dispersion stability to the DMF-based alumina suspension over a wide pH_a range. The zeta potential measurements indicate that PAA plays as "negative charge carriers" in this system to change the electrokinetic properties of alumina particles. As a result, the IEP of the alumina suspension can be shifted from approximately pH_a 7.6 to 3.2 with 2 wt% of the PAA concentration. The specific interaction energy between the alumina surface and dispersant PAA is -12.79 (RT units). The adsorption of PAA is detected using UV/vis spectroscopy, showing that the adsorption amount is markedly influenced by pH_a values, and that maximum adsorption occurs at pH_a 2.6. FTIR-ATR spectroscopy of the PAA-alumina complex gives further and detailed evidence of the interaction. The studies reveal that monodentate structure and hydrogen-bonded structure occur when $pH_a \leq 2.6$ and bidentate chelation is the main adsorption mechanism when $pH_a \geq 4$. Regarding the test results that the zeta potential of alumina particles, the adsorption amount and the interaction mechanisms are all intimately bound up with the suspension's pH_a values. The small dispersion difference over wide pH_a range was an unexpected result, but explained by a combination of static and different sizes of steric barrier induced by the configurational variation of PAA with the change of pH_a. Our experimental results lead to the conclusion that PAA can be an excellent electrosteric stabilizer in DMF solution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jeurceramsoc.2009.12.010.

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