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The role of organic dispersants in aqueous alumina suspensions

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Abstract

Several groups of organic compounds were investigated as potential dispersants for aqueous suspensions of micrometric aluminum oxide powder. They were compounds dissociating into bulky cations and small anions (tetralkylammonium chlorides and hydroxides, Methylene Blue), into bulky anions and small cations (phenols, mono- and poly-carboxylic acids, and fluorescein sodium salt), organic acids, and bases (tetralkylammonium hydroxides), and bulky, non-dissociating, polar compounds (Malachite Green and maltodextrin). We selected these compounds in order to contribute to the knowledge of how electrostatic interactions, the size and structure of the additive, and surface sorption onto alumina influence the rheological properties of colloidal alumina suspensions. We focused on low molecular weight additives, of different shape to influence interparticle electrostatic interactions as the most essential in reducing the shear stress at a given strain rate. The size and structure effects of these low molecular weight additives may be overshadowed by interparticle electrostatic interactions. In the case of non-dissociating macromolecules (e.g., maltodextrin), electrostatic interparticle interactions are minimal, and sorption is a principal factor influencing rheology.

Keywords: Al_2O_3; Suspensions; Dispersants; Rheology

1. Introduction

Successful colloidal processing of ceramics requires careful selection of organic plasticizers[1–3] to provide suitable plasticity, to prevent ceramic green bodies from cracking, and to limit distortions and volume contraction on drying and sintering. Some of these properties can be deduced from the rheological behavior and sedimentation as well as consolidation tests performed on aqueous powder suspensions. The rheology of metal oxide powder suspensions is controlled by several factors. They involve electrical double layer electrostatic stabilization which can be controlled by adjustment of the proportion of counteractive attractive and repulsion forces between particles in solution,[3–5] sorption of additives on powder surfaces (steric stabilization),[3–5] and solution disorder.[6] The impact of all these factors to the overall properties of suspensions results from a proper selection of suitable dispersants.

Based on well understood guidelines for selecting dispersants[7–9] we contribute with this paper to the knowledge of the role of the structure and physicochemical properties of dispersants in controlling the properties of suspensions for aqueous processing of alumina. It is well known that the structure of the electric double layer is the most important factor in the stabilization mechanism. The attractive part of interparticle interactions is usually determined by the nature of interacting particles and solvent, whereas the repulsive component of such interactions (e.g., steric stabilization) can be controlled by properties of dispersants. Among these properties, the size (a bulkiness) of admixed additives, the ability of these additives to sorb on powder particles and, as a consequence, the formation of an outer coordination sphere around alumina particles, as well as the acidity (basicity) responsible for either flocculation or deflocculation are obvious properties which should be maintained. In order to contribute to this problem, we performed studies on the dispersing properties of three groups of organic additives vary in size, charge localization and acidity (basicity).

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Alumina is a sorbent that is widely applied, for instance, in chromatography of inorganic and organic compounds.[10–14] Therefore, we focused on the results of the sorption of tested additives on alumina. The first group of tested additives dissociated into large cations with delocalised charge and small anions with localized charge [Methylene Blue (I), tetralkyl ammonium hydroxides (II–V), tetralkylammonium chlorides (VI–VII)]. It is likely that large cations should behave as Lewis acids with respect to the surface of alumina with the particles acting as a Lewis base. The Lewis acids are supposed to be immobilized on alumina whereas anions could be held by electrostatic attraction in the outer coordination sphere and are relatively mobile. Strongly basic tetralkylammonium hydroxides increased the pH of solutions above 9 and introduced additional modification to the structure of aqueous alumina suspensions by hindering flocculation of the suspensions.

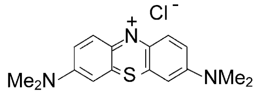
Additives in the second group represent compounds that dissociate into small cations (Lewis acids capable of sorption on alumina surface) and large anions [fluorescein sodium salt (VIII), phenol (IX), 1-naphthol (X), 2-naphthol (XI), and phloroglucinol (XII), dioic saturated (XIII–XVII), and unsaturated (XVIII–XIX), trioic (XX), and tetrioic acids (XXI)]. Finally, we investigated the effect of a third group of additives [Malachite Green (XXII) and maltodextrin 040 (3.6 kDa) (XXIII)]. They were non-dissociating sorbates. In contrast to Malachite Green (XXII) providing a real solution, maltodextrin (XXIII) solubilised in water forming colloidal solutions. Effects of maltodextrin (XXIII) on the rheological properties of aqueous alumina suspensions have been previously investigated.[15–22]

Mazurkiewicz et al.[6] previously showed that bulky species of various salts significantly decreased the viscosity of aqueous solutions by introducing structural disorder. Based on these results, we assumed that the applied additives, particularly when applied in excess, should introduce disorder into aqueous solutions, and as a result, these additives might decrease the viscosity of aqueous suspensions of aluminum oxide powder.

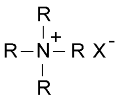
2. Experimental procedure

2.1. Materials

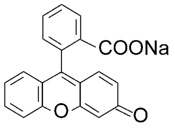
Fluorescein sodium salt, Methylene Blue, Malachite Green, and all tetralkylammonium compounds were purchased from Sigma Corporation (St. Louis, MO, USA). Phenol, both isomeric naphthols, phloroglucinol, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, tricarballylic acid, and 1,2,3,4-butanetetracarboxylic were products of Aldrich Chemical Company, Inc., Milwaukee, WI, USA. Maltodextrin (Maltrin 040 of average molecular weight of 3600 g/mole) was the product of Grain Processing Corp., Muscatine, IA, USA. Alumina powder (α-Al_2O_3 of equiaxial particle shape, average particle size of 0.4 μm, and specific surface area of 8.5 m^2/g) was the product of Alcoa Corporation (Bauxite, AR, USA).



I


$\mathrm{R-\overset{R}{\underset{R}{N^+}}-R\ X^-}$

X = OH, R = Me II
R = Et III
R = n - Pr IV
R = n - Bu V
X = Cl R = n - Pr VI
R = n - Bu VII



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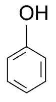
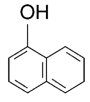


IX



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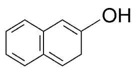
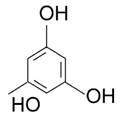
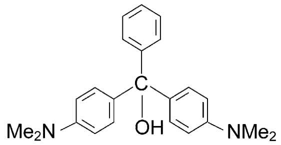


XI



XII



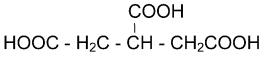
XIII

HOOC - $(CH_2)_n$ - COOH

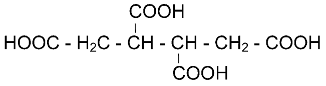
n = 0 XIV
n = 1 XV
n = 2 XVI
n = 3 XVII
n = 4 XVIII

HOOC - CH = CH - COOH

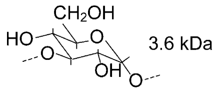
cis XIX
trans XX


$\mathrm{HOOC - H_2C - \overset{COOH}{CH} - CH_2COOH}$

XXI


$\mathrm{HOOC - H_2C - \overset{COOH}{CH} - \underset{COOH}{CH} - CH_2 - COOH}$

XXII



XXIII

2.2. Alumina suspensions with additives

Aqueous solutions 1.37×10^{-3} M (162 ml) of a given additive (I–XXII) were prepared, and alumina powder (156 g) was subsequently added to each solution. In addition, solutions (162 ml) of fluorescein sodium salt (VIII), with concentrations of 2.74×10^{-3} and 5.48×10^{-3} M solutions were prepared and subsequently mixed with (156 g) alumina powder. All suspensions were placed in sealed, plastic bottles and agitated on a shaker for 24 h. The pH of the suspension of alumina with no additive measured after such equilibration was 8.78.

2.3. Rheometry

A couette rheometer (RheoStress RS 75, Gebrueder Haake GmbH, Karlsruhe, Germany) was used to determine rheological properties of all suspensions at 20 °C. Each suspension was subjected to an increasing shear rate starting at 0 s^{-1} increasing to 500 s^{-1} The shear rate was subsequently reduced to 0 s^{-1}. All measurements were duplicated on the same sample.

2.4. Sedimentation test

Gravity sedimentation tests were performed by pouring 100 ml of a given suspension into a 100 ml graduated Pyrex glass cylinder. Sediment heights were recorded as a function of time.

2.5. Centrifugation

Suspensions (approximately 25 g) were centrifuged at 4000 rpm for 1 h in a Beckman™ tabletop centrifuge model GS-15 with swinging rotor. We performed centrifugation measurements for various time periods and determined that 1 h at 4000 rpm was sufficient for the specimens to reach an equilibrium cake height. The centrifugation tubes were flat-bottomed acrylic tubes measuring 2.54 cm inside diameter by 10 cm tall. The typical distance from the rotation axis to the bottom of the centrifugation tube was 13.17 cm.

2.6. Slip casting

Suspensions were slip cast onto a flat surface of a plaster mold. Cylindrical pellets were formed by firmly placing a flat sheet of acrylic (5.4 mm thick) onto this plaster mold and then pouring suspension into an array of circular holes (14.3 mm diameter) previously drilled through the acrylic sheet. The pellets were subsequently dried in open air for 24 h. The dried pellets subsequently underwent sintering in open air. The sintering schedule involved a slow increase in temperature to a maximum temperature of 1050 °C, which was maintained for 3 h prior to a slow decrease to room temperature. Upon cooling, each specimen underwent density measurements by the use of water immersion and the Archimedes principal.

2.7. Cross-experiments with fluorescein sodium salt and maltodextrin 040

1. Alumina powder (312 g) was suspended in a solution of maltodextrin 040 (9.36 g) in deionized water (190 ml) and then equilibrated on the shaker for 24 h. Immediately thereafter, a 10% aq. solution of fluorescein sodium salt (5 ml) was added and equilibrated on the shaker for another 24 h. The resulting suspension was subsequently analyzed by rheometry, sedimentation, centrifugation, as described above.
2. Alumina powder (312 g) was suspended in a 10% aq. solution of fluorescein sodium salt (5ml) diluted with deinonized water (190 ml) and then equilibrated on a shaker for 24 h. Immediately thereafter, maltodextrin 040 (9.36 g) was added and equilibration by shaking was continued for another 24 h. The resulting suspension was subsequently analyzed by rheometry, sedimentation, centrifugation, as described above.

2.8. Fluorescence spectra

In order to prove sorption of maltodextrin on alumina, fluorescence spectra were measured on alumina specimens prepared with fluorescein and maltodextrin as described above. These measurements were performed in the region of 450–620 nm at 4 K for wet cakes that were centrifuged by the method described above. In addition, we measured fluorescence spectra on aqueous solutions of fluorescein. The McPearson Monochromator with Princeton Instrument optical multianalyser for optical detection and Lambda Physics Excimer Pumped Dilaser for fluorescence excitation were used.

3. Results and discussion

Table 1 summarizes the rheological measurements of 20 vol.% alumina suspensions that were prepared with various organic additives. In the absence of any organic additive, highly flocculated behavior was observed. In this case, the shear stress reached 40 Pa at a strain rate of 500 s^{-1}. This property was modified to a various extent by applied additives.

Methylene-blue (I) dissociated into a large, almost planar cation and small anion. Because of resonance the positive charge in the cation was delocalised. Addition of (I) seemed to increase flocculation. Shear stress, τ, significantly increased and it was accompanied by a high viscosity of the suspension. Probably, there was a strong adsorption of (I) on alumina and accompanied chloride anions could additionally increase the ordering of the solvent in suspension. Apart from the chloride anion, dissociation of tetraalkylammonium chlorides (VI and VII) produced large, ball-like cations in which the positive charge was well hidden in the cation center. Because the pH of the solutions was around 8.8 one could assume weak interactions between particular cations acting as weak Lewis acids and hydroxyl groups of alumina in which lone electron pair orbitals were the sites of the Lewis basicity.

Both tetraalkylammonium cations slightly reduced the measured shear stress in suspensions. The larger tetra-*n*-butyl ammonium cation was more effective in decreasing the shear stress. The viscosity of suspensions

Table 1
Rheology of 20 vol.% alumina suspensions containing various additives[a]

Additive	τ^{20}	τ^{50}	τ^{100}	τ^{200}	τ^{500}	η^{50}	η^{100}	η^{200}	η^{500}
None	13	19	28	35	40				
Methylene Blue (I)		35		40	48	0.74		0.22	0.1
Tetraakylammonium hydroxides									
Tetramethyl (II)		11		14	18.6	0.22		0.06	0.04
Teteraethyl (III)		12		15	19.6	0.24		0.08	0.045
Tetra-*n*-propyl (IV)		11.2		14	18.4	0.23		0.08	0.04
Tetra-*n*-butyl (V)		11		14	18.4	0.20		0.08	0.04
Tetraakylammonium chlorides									
Tetra-*n*-propyl (VI)		21.5		27	34	0.43		0.14	0.07
Tetra-*n*-butyl (VII)		17		22	28	0.34		0.12	0.06
Phenols									
Fluorescein (VIII)		20		26	33	0.44		0.1	0.08
Phenol (IX)		16		20	25.6	0.33		0.12	0.06
1-Naphthol (X)		21.5		26	33	0.50		0.15	0.07
2-Naphthol (XI)		21		26	34	0.42		0.10	0.08
Phloroglucinol (XII)		6.4		8	10.9	0.12		0.04	0.02
Carboxylic acids									
Oxalic (XIV)	18		21		30		0.2		0.07
Malonic (XV)	21		27		37		0.28		0.08
Succinic (XVI)	28		35.5		46		0.33		0.1
Glutaric (XVII)	28		35		46		0.33		0.1
Adipic (XVIII)	28		36		47		0.36		0.1
Maleic (XIX)	22		30		42		0.30		0.1
Fumaric (XX)	26.5		33		44		0.35		0.1
Tricarballylic (XXI)	14		19		27		0.18		0.05
Butanetetracarboxylic (XXII)	1.4		1.6		6.8		0.18		0.014
Non-ionized additives									
Malachite Green (XXII)		17.5		19	23.5	0.35		0.15	0.002
Maltodextrin 040 (XXIII)	0.1	0.25	0.3	0.7	1.6				

[a] τ represents shear stress in Pa, and η represents viscosity in Pa s. The superscripts to the right of τ and η represent the shear rate in s^{-1}.

clearly decreased, possibly, because of strong disorder in the solution introduced by bulky, poorly sorbed tetraalkylammonium cations. Again, the more bulky tetra-*n*-butylammonium cation was more efficient in this respect. Dissociation of tetraalkylammonium hydroxides (II–V) produced similar bulky, ball-like cations as (VI) and (VII). However, because the addition of these extremely strong bases raised the pH above 9 and, in consequence, the proton from the hydroxyl groups of alumina was abstracted,[23] a strong charge-to-charge interaction ($Al–O^{-}\ldots cation^{+}$) took place. Under such circumstance, the shear stress under low and high shear rates and the suspension viscosity were reduced. It could be seen that, in contrast to tetraalkylammonium chlorides where the size of cation had a recognizable effect, the size of cation was practically insignificant in this case.

The second group of additives contained compounds that, on dissociation, produced proton(s) and larger anions. Compounds from these groups can be grouped into phenols being weaker acids and producing planar (almost planar in the case of fluorescein) anions and carboxylic acids being stronger acids as phenols and producing flexible carboxylate anions. The effect of phenols as well as low-molecular carboxylic acids as dispersants have been formerly recognized by Gauckler et al.[7,24–26] Therefore, in our studies we did not focus on the adjustment of the proper dose for these types of additives in order to achieve a maximum effect. We assumed that operation below the dose of such additives suitable for full deflocculation would be beneficial in order to observe the effects of the shape and volume of the additive molecule.

Both types of dispersants were proton donors and, therefore, protonation of the hydroxyl groups of alumina generated the surface charge on alumina particles. Phenols (IX–XII) were weak acids with pK_a in water at 25 °C ranging from 10.0 to 8.0.[27,28] On comparison of shear stress after admixture of either phenol, both isomeric naphthols, or very bulky fluorescein (VIII), the effect of the size and shape of phenolate anion could be seen. Roughly, one could state that the larger the anion, the weaker its dispersive ability. Among phenols, phloroglucinol (XII) had a remarkable effect upon shear stress

Table 2
$pK_{a,\ H_2O}$ of phenols and carboxylic acids in water at 25 °C[27,29]

Additive	pK_a		
	1	2	3
Phenols			
Phenol	10.0		
1-Naphthol[a]	9.85		
2-Naphthol[a]	9.63		
Phloroglucinol[a]	7.97	9.23	
Carboxylic acids			
Oxalic	1.27	4.27	
Malonic	2.86	5.69	
Succinic	4.21	5.64	
Glutaric	4.34	5.27	
Adipic	4.42	5.28	
Maleic	3.02	4.38	
Fumaric	1.92	6.23	
Tricarballylic	3.48	4.50	5.82
Butanetetrioic	4.06		

[a] Data is related to 20 °C.

and viscosity. In this case its pH reducing, deflocculating effect on the alumina suspension played a dominating role. Its addition reduced pH from 8.78 to 6.3. The effect of the pK_a of carboxylic acids (Table 2) upon the shear rate and viscosity of suspensions seemed to express intervention of their acidity, in general, but also the size of anion and, first of all, deflocculating ability of the admixed acids.

The addition of (XXII) lowered the suspension pH to 3.74, and the pH of suspension with (XXI) was approximately 4.5. The strongest among the tested acids, (XIV), reduced the shear stress to almost the same extent as the much weaker (XXII), and the addition of (XXIII) gave a superior result. Three acids (XVI–XVIII) with almost identical pH similarly affected the shear stress. The factor of the carboxylate anions seemed to be practically not important, possibly because of the flexibility of the anions. Comparison of the effects of isomeric (XX) and (XIX) being *trans*- and *cis*-isomers, respectively, showed that from the rheological point of view the smaller anion of (XIX) was slightly more beneficial than the larger (longer) anion of (XX). Comparison of the effects of admixture of small molecules of (XIV) and large molecules of (XXII) pointed to the deflocculating ability as that of the primary importance.

The triphenylmethane dye (XXII) from the third group of tested dispersants resided in the alumina suspension in the form of non-dissociated leucobase. The effect of this additive upon shear stress and viscosity should be interpreted as the result of poor sorption on alumina particles and structural disorder introduced to the solution by this large, bulky compound.

The effect of the addition of maltodextrin (XXIII) of 3.6 kDa required special consideration. Maltodextrin is a charge-free macromolecule, which produces a colloidal solution on its solubilisation in water.[30] In view of the assumption of poor sorption of (XXII) on alumina, sorption of (XXIII) on this sorbent required proof. Sorption of (XXIII) on alumina received confirmation in cross experiments with (VIII). The addition of (XXIII) to alumina suspensions significantly reduced the shear stress at a given strain rate by its sorption on alumina. We observed a significant reduction of the shear stress of alumina–fluorescein blends upon the addition of maltodextrin.

In contrast, the addition of fluorescein to alumina–maltodextrin suspensions did not produce any significant changes in rheology. It is well known from chromatographic separation techniques that fluorescein sorbed on alumina. In Table 1, the addition of fluorescein slightly reduced the shear stresses at a given strain rate compared to alumina suspensions containing no additive. Thus, one could conclude that these reductions in shear stress were produced by sorption. The subsequent addition of maltodextrin, however, reduced the shear stresses even more. In the following paragraphs, we showed that this was caused by desorption of fluorescein and sorption of maltodextrin instead.

Fluorescein in aqueous solution without alumina exhibited two maxima located at 490 and 498 nm. Upon the subsequent addition of alumina and centrifugation of wet cakes, the bands at 490 and 498 nm vanished,

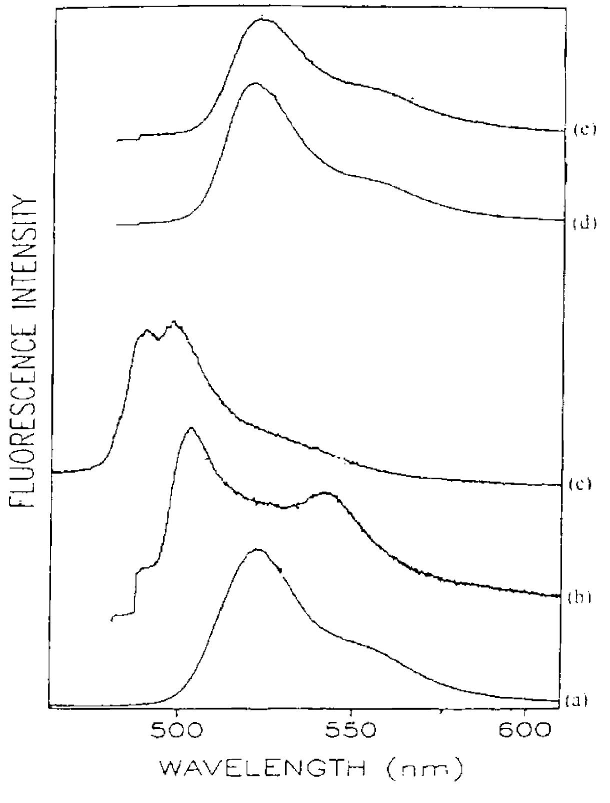


Fig. 1. Fluorescence spectra of: (a) dried centrifuge cake of alumina with fluorescein, (b) wet centrifuge cake of alumina with fluorescein, (c) fluorescein in aqueous solution without alumina, (d) wet centrifuge cake of alumina with fluorescein after the addition of maltodextrin, and (e) wet centrifuge cake of alumina with maltodextrin after the addition of fluorescein.

and bands at 503 and 543 nm appeared (Fig. 1). This provided evidence for interactions between fluorescein and alumina. The UV spectrum of the alumina–maltodextrin blend, after the addition of fluorescein showed two bands at 523 and 560 nm. The spectral pattern and position of the band in the UV spectrum of the alumina–fluorescein blend did not change after the addition of maltodextrin. This was evidence for desorption of fluorescein from alumina upon the addition of maltodextrin.

In strong contrast with other additives, the addition of (XXIII), the molecular size of which was larger by several orders than the size of other tested additives, produced the most fluid suspension compared with all other specimens in this study. In the case of the maltodextrin additive, alumina suspensions exhibited Newtonian-like behavior with a nearly linear increase in shear stress as a function of shear rate. In this case, the maximum shear stress reached of 1.6 Pa at 500 s^{-1}. This effect showed that the addition of dispersants providing colloidal character at pH >8 might be an alternative approach to processing of aqueous micrometric alumina suspensions. There were successful applications of such polyelectrolytes for this purpose as poly(acrylic acid) and poly(methacrylic acid), which offered colloidal character of suspensions with a simultaneous decrease in pH[31–33] as well as a joint use of citric acid with poly(vinyl alcohol).[34]

As shown in Table 3, the degree of consolidation was generally poor in all sedimentation tests but that with (XXIII). During sedimentation tests, all suspensions exhibited flocculated behavior, from the standpoint that supernatants were transparent to the naked eye. The highest degree of sedimentation was observed for (XII), which as shown in Table 1, also exhibited a relatively low shear stress at a given strain rate. Slip cast densities were approximately 50–53 vol.% alumina, regardless of the organic additive used. All of the slip cast pellets, except those from (XXI), (XII), and acid (XX) exhibited cracking upon drying. Exceptional consolidation and rheological behaviour of (XXIII) was described in our former papers.[15–22]

Table 3
Effects of organic additives on alumina sediment volumes and densities of slip-cast alumina pellets

Additive	Sediment volume (ml)	Alumina concentration in slip cast pellet (vol.%)
Methylene Blue (I)	100	52.0
Tetraalkylammonium hydroxides		
Tetramethyl (II)	87	54.0
Tetraethyl (III)	87	52.4
Tetra-*n*-propyl (IV)	84.5	49.8
Tetra-*n*-butyl (V)	86	
Tetraalkylammonium chlorides		
Tetra-*n*-propyl (VI)	93.5	49.6
Tetra-*n*-butyl (VII)	92.5	
Phenols		
Fluorescein (VIII) (5 g)	89.5	53.0
(2.5 g)	89	53.4
(1.25 g)	92.5	53.2
Phenol (IX)	88.5	51.1
1-Naphthol (X)	86.5	
2-Naphthol (XI)	90.5	
Phloroglucinol (XII)	80.5	52.0
Oxalic acid (XIII)	94.5	
Malonic acid (XIV)	98	
Succinic acid (XV)	98	
Glutaric acid (XVI)	99	
Adipic acid (XVII)	98	
Maleic acid (XVIII)	97.5	
Fumaric acid (XIX)	98.5	
Tricarballylic acid (XX)	98	
1,2,3,4-Butanetetracarboxylic acid (XXI)	85	
Malachite Green (XXII)	92	51.3
Maltodextrin 040 (XXIII)	20	

4. Conclusions

In the case of low-molecular-weight additives, interparticle electrostatic interactions are most essential in reducing the shear stress at a given strain rate. The small size of these low molecular weight additives is beneficial for reducing the shear stress, but this effect may be overshadowed by interparticle electrostatic interactions. In the case of non-dissociating macromolecules sorption is a principal factor influencing rheology.

Acknowledgement

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