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Influence of the Dispersant Structure on Properties of Electrostatically Stabilized Aqueous Alumina Suspensions

Pirmin C. Hidber,* Thomas J. Graule & Ludwig J. Gauckler

Nichtmetallische Werkstoffe, Eidgenössische Technische Hochschule, ETH Zentrum, CH-8092 Zürich, Switzerland

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Abstract

A series of molecules based on a benzene ring substituted with (-OH) and (-COOH) groups was used to derive guidelines for the selection of dispersants for a given colloidal forming process. The relation between the molecular structure of low-molecular-weight organic dispersants and their influence on the properties of α*-*Al_2O_3 *suspensions was studied. In particular, the effect of the nature, number and position of the functional groups attached to the benzene ring on the adsorption behaviour of these molecules on* α*-*Al_2O_3 *and on the electrophoretic mobility of alumina particles in aqueous suspension has been examined. The effect of a low-molecular-weight dispersant is mainly determined by its ability to adsorb on the powder surface and by the number of functional groups that can dissociate and act as surface-charge modifiers. The maximum degree of adsorption for any given dispersant was found in the pH range corresponding to the pKa value of its functional group. High adsorption ability and high efficiency over a wide pH range could be achieved for a single dispersant by combining several functional groups of different pKa values in the same molecule. Adsorption of a dispersant was promoted strongly by chelate ring formation with the powder surface. The efficiency of the dispersants increased with increasing number of charge carriers per molecule, provided that adsorption behaviour was otherwise similar. © 1996 Elsevier Science Limited.*

1 Introduction

The key element in colloidal processing of ceramic powders is control over the interparticle forces within the suspension during all stages of processing. Certain steps in wet-powder processing depend on repulsive forces between the particles, whereas other steps may require attractive ones.[1] Organic and inorganic dispersants are widely used to control the interparticle potential.[2-10] By adsorbing onto the surface of the powder, these surface-active chemicals increase the repulsive interaction between the powder particles, by increasing the particle charge and/or by building up a steric barrier between the particles. An understanding of the mechanism of their interaction with the powder surface in different pH regimes is therefore essential to improve the quality of the ceramics produced by colloidal processing methods.

Studies of the dispersant–powder particle interaction have shown the phenomenon to be complex.[11-13] A number of factors such as pH, ionic strength, dispersant structure, reduction of conformational entropy during the adsorption process, dispersant solubility, powder surface composition and temperature have all proved to be important. The aim of this study is to correlate the efficiency of organic dispersants with their molecular structure. The present study is restricted to dispersants with a small molecular weight. We have chosen, as model compounds, dispersants containing a benzene ring with different substituents (Table 1). We have selected these compounds because their geometry is well defined due to the rigidity of the aromatic ring. We have examined the effect of the nature, number and position of the benzene ring's functional groups on the properties of aqueous alumina suspensions. The adsorption behaviour of these molecules on alumina is discussed, along with their influence on the electrophoretic mobility of the alumina particles. We have also demonstrated that the principles derived from the study of aromatic dispersants can be applied to the use of aliphatic compounds.

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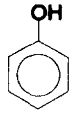
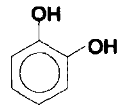
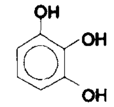
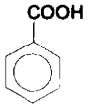
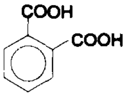
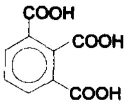
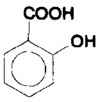
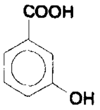
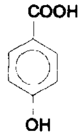
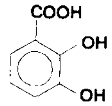
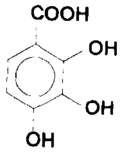
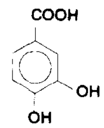
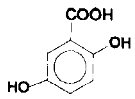
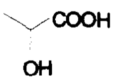
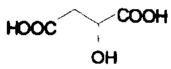
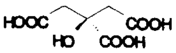
*Present address: Harvard University, Department of Chemistry, 12 Oxford St., Cambridge, MA 02138, USA.

Table 1. Compounds used in the adsorption and mobility experiments

Compound	*pKa value*	*Structure*
Phenol	9·82	
1,2-Dihydroxybenzene (catechol)	(13), 9·24	
1,2,3-Trihydroxybenzene (pyrogallol)	(14), 11·08, 8·94	
Benzoic acid	4·00	
Phthalic acid	4·92, 2·75	
Hemimellitic acid	5·51, 3·82, 2·62	
2-Hydroxybenzoic acid	13·4, 2·81	
3-Hydroxybenzoic acid	9·68, 3·96	
4-Hydroxybenzoic acid	8·95, 4·36	
2,3-Dihydroxybenzoic acid	(13·1),10·06, 2·70	
2,3,4-Trihydroxybenzoic acid	?,12·3, 8·7, 3·2	
3,4-Dihydroxybenzoic acid	(11·7), 8·83, 4·32	
2,5-Dihydroxybenzoic acid	12·74, 10·00, 2·70	
Propionic acid	4·63	
Lactic acid	?, 3·66	
Malic acid	?, 4·68, 3·2	
Citric acid	?, 5·82, 4·5, 3·48	

The pKa values are listed for an ionic strength of 0·1 and a temperature of 25°C.[31] pKa values that are assumed to be greater than 14 are labelled with '?'

The effect of dispersants with a small molecular weight (such as those used in the present study) is mainly based on the buildup of a high surface charge. (In the following, we treat the alumina particle and its adsorbed layer as a single unit. The term 'surface charge' should also be understood in this sense). The dispersants adsorb on the particle surface as singly or multiply charged ions, leading to a change in the surface charge. The steric hindrance caused by the adsorption of these small molecules on the powder surface can be neglected, except at very small particle–particle separation and/or low surface potentials. The effect of these dispersants is determined both by the number of ionizable groups and by adsorption behaviour. The number of dissociable groups in a given dispersant molecule determines the change of the surface charge per adsorbed molecule. The distribution of the dispersant between the liquid phase and the particle surface (i) influences the ionic strength (and thereby the zeta potential) and (ii) determines the number of adsorbed molecules (and thereby the change in surface charge). We have shown previously that the careful choice of the dispersant concentration allows the surface charge, the IEP and the viscosity of the suspension to be adjusted to the requirements of a given forming process.[9] We note that a maximum zeta potential does not necessarily result in the lowest possible suspension viscosity for any given solid content,[14] and can lead to a low green density.

At this point, we wish to emphasize that there is as yet no ideal dispersant for all wet ceramic processes. Whereas for one ceramic process, a dispersant might be effective in a very defined and limited pH region, another process might need a dispersant for a wide pH range. In one case, maximum adsorption of the dispersant on the powder surface may be required, in another case only partial adsorption might be desirable. The intent of this study can therefore not be to design the most efficient dispersant, but rather to develop criteria for the selection of a dispersant for a specific process.

2 Experimental Procedures

2.1 Materials

2.1.1 Alumina

We used a high-purity α-Al_2O_3 powder (HRA10, Martinswerk Bergheim, Germany) with a mean particle size of 0·5 μm and a BET surface area of 10 m^2/g. The powder purity exceeded 99·99%, containing (in ppm) < 30 Na_2O, < 50 SiO_2, < 12 Fe_2O_3 and < 8 MgO. Prior to use, the alumina was cleaned by an acidic washing process. The isoelectric point (IEP) for the α-Al_2O_3 used in this investigation is 9·2 (9·3) determined by acid/base titration at different ionic strengths (dynamic electrophoretic mobility measurements).[15] These values correlate well with the zero point of charge (ZPC) values reported for α-Al_2O_3 powder.[16] For the maximum exchange capacity of surface AlOH groups $\{AlOH\}_t$, i.e. the maximum number of surface hydroxyl groups that can be protonated or deprotonated, we obtained a value of 2·56 (–OH) groups/nm^2 (42·5 mmol/kg);[15] this agrees with the value of 2·7 (–OH) groups/nm^2 reported by Huang,[17] but is much less than the 6 (–OH) groups/nm^2 estimated from crystal lattice considerations.[18] The reason for this difference is that an increasing surface charge prevents the (de)protonation of all hydroxyl groups present on the surface.

2.1.2 Organic reagents

Unlabelled organic compounds were obtained from Fluka AG, Buchs, Switzerland and were used without further purification. ^{14}C-labelled propionic acid, lactic acid, malic acid and citric acid were obtained from Amersham, Buckinghamshire, UK.

2.1.3. Inorganic reagents

All suspensions were prepared using high-purity water (specific electrical resistance > 20 MΩ cm). The pH values were adjusted with HNO_3 or KOH (Titrisol, 0·1 N and 1 N, respectively, Merck, Darmstadt, Germany). KNO_3 (MicroSelect) used for adjusting the ionic strength was purchased from Fluka AG, Buchs, Switzerland.

2.2 Methods

Unless otherwise indicated, all concentrations are given in weight percent (wt%) relative to the solid content. The pH of the suspension was measured with a combined glass electrode (Metrohm AG, Herisau, Switzerland).

2.2.1 Adsorption curves

Forty millilitres aqueous organic acid solution (1 mM, inert electrolyte 0.1 M KNO_3), an aliquot of HNO_3 or KOH and alumina (3 g) were placed in 50 ml polypropylene centrifuge tubes. In the case of aliphatic compounds, a small amount of the corresponding ^{14}C-labelled molecules was also added. The concentration of the labelled molecules was insignificant compared to the total dispersant concentration, i.e. < 1%. The tubes were sealed and turned end-over-end (5 rpm) in a dark, thermostatted cabinet at 25°C for 48 h. Next, the pH of the suspensions was measured. After centrifugation

(4500 *g* for 90 min), the concentrations of the aromatic compounds in the supernatant were determined by UV spectroscopy. In the case of aliphatic molecules (propionic acid, lactic acid, malic acid and citric acid), the concentration of the acid in the supernatant was determined using ^{14}C-techniques.[19] The adsorption was calculated from the difference between the amount of dispersant added and that remaining in the supernatant.

2.2.2 Measurement of the electrokinetic properties

The measurements of the ESA signal as a function of the pH value were performed for 3 vol% alumina suspensions using a Matec ESA-8000 instrument (Matec Applied Sciences, Hopkinton, MA, USA). At this solid loading, the relation between the ESA signal and the dynamic electrophoretic mobility is still linear.[15] The SP-80 ESA probe was calibrated using 10 vol% Ludox TM (Du Pont, Wilmington, DE, USA) in water. The ESA value for the Ludox solution was taken to be −5·32 mPa m/V at 25°C.[20] All measurements were performed at 25°C ± 0·2°C. The apparatus was calibrated before each titration, and was checked after completion of the measurement. The value of the Ludox reference solution measured after the titration was within ± 3% of the original value. Before use, the suspensions were ultrasonicated for 4 min. Potentiometric titration of the suspensions with either HNO_3 or KOH solution (0·1 M or 1 M) was performed automatically, with a delay time of 45 s.

The magnitude of the ESA signal is related to the dynamic electrophoretic mobility, μ_d, of the particles by:[21]

$$\mathrm{ESA}(\omega) = \mu_d(\omega)\cdot c\cdot \Delta\rho\cdot \Phi\cdot G_f \qquad (2.1)$$

where $\mu_d(\omega)$ is the electrophoretic mobility, c is the sound velocity in the suspension, $\Delta\rho$ is the density difference between the particles and the solvent, Φ is the volume fraction of the particles, G_f is a geometrical factor for the electrode geometry and ω is the angular frequency of the applied field.

3 Results and Discussion

3.1 Aromatic compounds

3.1.1 Hydroxyl groups

In Fig. 1 the adsorption of phenol, catechol and pyrogallol on α-Al_2O_3 is plotted in 'percent of the added amount' versus the pH of the suspension. Phenol, with only one hydroxyl group, shows no adsorption within the detection limits. The presence of a second hydroxyl in the ortho position (catechol), allowing the formation of a chelate surface complex, drastically changes the adsorption behaviour. At pH 4, 10% of the added amount of catechol is adsorbed, increasing to almost 80% at pH 9. Even better adsorption is observed when three hydroxyl groups are present (pyrogallol).

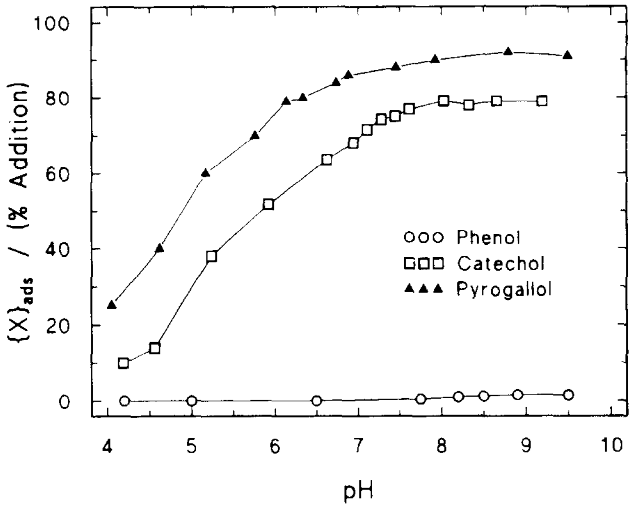


Fig. 1. Adsorption curves of phenol, catechol and pyrogallol on α-Al_2O_3. The lines are intended as a guide to the eyes.

Figure 2 shows the influence of these three molecules on the electrophoretic mobility of α-Al_2O_3. We note that we are comparing the influence of the dispersant molecule based on the amount added and not on the adsorption density of the dispersant. Phenol does not apparently influence the electrophoretic mobility of the particles. This behaviour is to be expected, since phenol does not adsorb on the alumina surface at all. The addition of catechol leads to a shift of the IEP of over 1·5 pH units and to a negative surface charge in the pH range from 8 to 11. Pyrogallol influences the electrophoretic mobility–pH curves

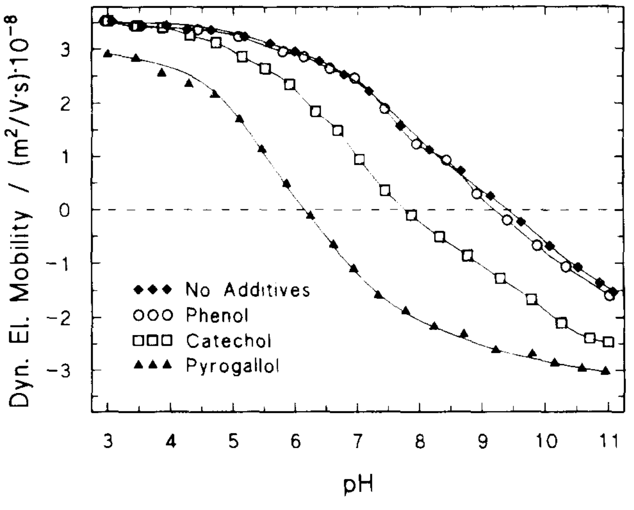


Fig. 2. Influence of phenol, catechol and pyrogallol on the dynamic electrophoretic mobility of alumina particles. The lines are intended as a guide to the eyes.

even more strongly: The positive surface charge is further diminished and the IEP is shifted to pH 6·2. We note that the first two dissociation steps of pyrogallol occur at slightly lower pKa values than those of catechol (Table 1). This probably also contributes to the greater effect of pyrogallol, especially in the low pH regime (Section 3.3).

3.1.2 Carboxyl groups

The adsorption curves of benzoic acid, phthalic acid and hemimellitic acid on alumina are shown in Fig. 3. As we have seen before, the adsorption increases with the number of functional groups per molecule. Benzoic acid has a relative pronounced adsorption maximum around pH 4·3. This adsorption maximum becomes broader with increasing number of carboxyl groups in the molecule (phthalic and hemimellitic acid). Whereas the hydroxyl derivatives adsorbed preferentially in the high-pH regime, the carboxylic acids showed strong adsorption in the low-pH region.

As one would expect from the adsorption curves, benzoic acid barely influences the electrophoretic mobility of the alumina particles (Fig. 4). The presence of a second carboxyl group in the molecule (phthalic acid) results in a decrease of the surface charge in the entire pH range, as well as in a shift of the IEP by 2 pH units to lower values. The reasons for the greater influence of phthalic acid are the same as those already described for the hydroxyl derivatives: (i) increased adsorption of phthalic acid on alumina and (ii) the presence of a second dissociable group. The importance of the number of dissociable groups becomes even clearer when we compare the influence of phthalic and hemimellitic acids on the electrophoretic mobility. Both the greater shift of the IEP and the higher negative surface charge in the range 3 < pH < 7 could be a consequence of either the number of dissociable groups or the increased adsorption ability of the hemimellitic acid. However, the higher negative surface charge induced by hemimellitic acid in the range 7 < pH < 10 can only be attributed to the additional carboxyl group, since the adsorption of hemimellitic acid in this pH range is actually slightly smaller than that of phthalic acid.

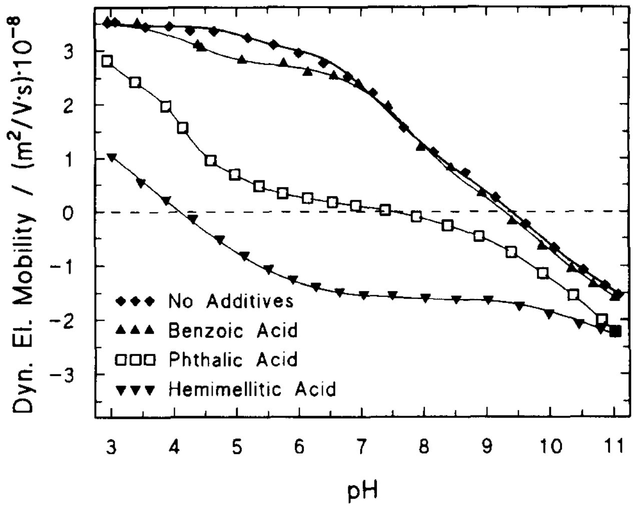


Fig. 4. Influence of benzoic acid, phthalic acid and hemimellitic acid on the dynamic electrophoretic mobility of alumina particles. The lines are intended as a guide to the eyes.

3.1.3 Combination of hydroxyl and carboxyl groups

Figure 5 shows the adsorption of 2-, 3- and 4-hydroxybenzoic acid on alumina as a function of pH. The adsorption behaviour of 3- and 4-hydroxybenzoic acid is similar to that of benzoic acid. 2-Hydroxybenzoic acid, however, shows an adsorption curve that is completely different

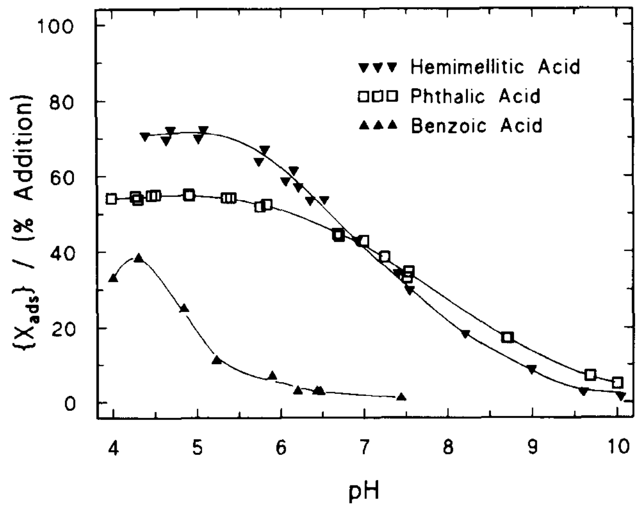


Fig. 3. Adsorption curves of benzoic acid, phthalic acid and hemimellitic acid on α-Al_2O_3. The lines are intended as a guide to the eyes.

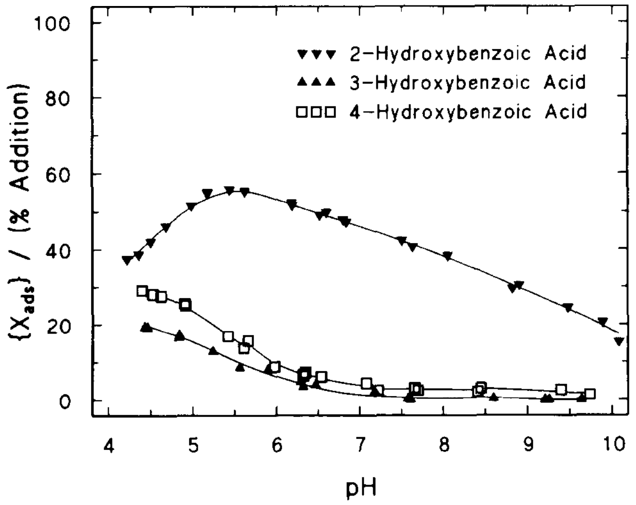


Fig. 5. Adsorption curves of 2-, 3- and 4-hydroxybenzoic acid on α-Al_2O_3. The lines are intended as a guide to the eyes.

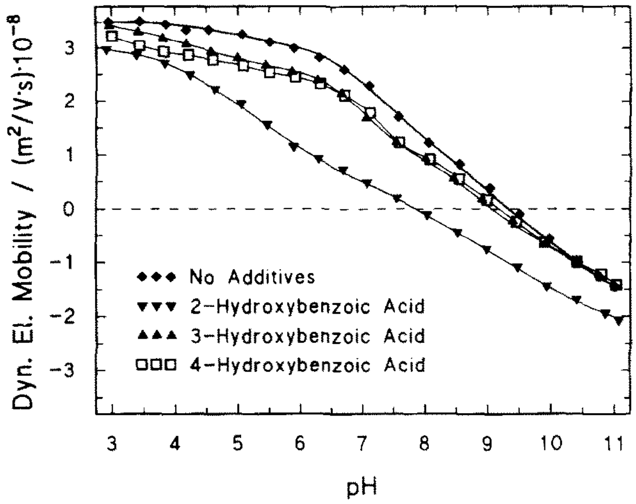


Fig. 6. Influence of 2-, 3- and 4-hydroxybenzoic acid on the dynamic electrophoretic mobility of alumina particles. The lines are intended as a guide to the eyes.

compared to that of either phenol or benzoic acid. Starting at 40% at pH 4, the adsorption goes through a maximum at pH 5·5, decreasing to about 15% at pH 10. These differences are also reflected in the influence of the three molecules on the electrophoretic mobility of alumina (Fig. 6). The only significant shift of the IEP (2 pH units) is caused by 2-hydroxybenzoic acid.

The influence of the number of hydroxyl groups in a benzoic acid molecule on its adsorption behaviour is illustrated by comparing the adsorption of benzoic, 2-hydroxy-, 2,3-dihydroxy- and 2,3,4-trihydroxybenzoic acids (Fig. 7). At pH 4, the adsorption of all four compounds is similar. With increasing pH, however, differences become evident. The adsorption density at higher pH values is influenced by the number of hydroxyl groups per molecule. The more hydroxyl groups that are present in a molecule, the higher is the adsorption density in the neutral and alkaline pH region. 2,3,4-Trihydroxybenzoic acid with three hydroxyl groups shows almost complete adsorption above pH 5. The differences in the adsorption ability and the number of dissociable groups are reflected in the influence of these molecules on the IEP and on the electrophoretic mobility curves of alumina (Fig. 8).

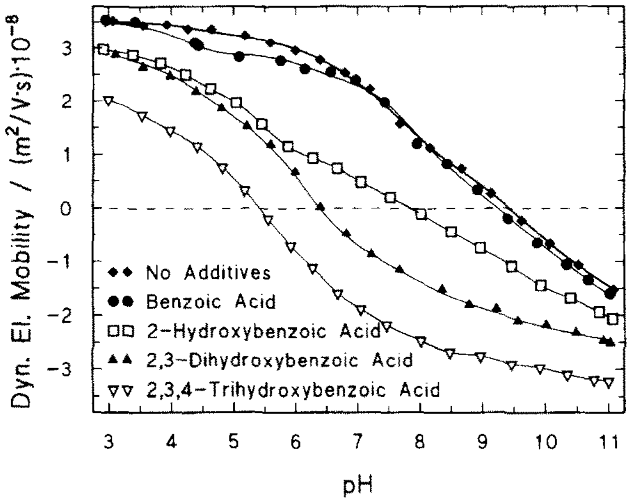


Fig. 8. Influence of benzoic acid, 2-hydroxy-, 2,3-dihydroxy and 2,3,4-trihydroxybenzoic acid on the dynamic electrophoretic mobility of alumina particles. The lines are intended as a guide to the eyes.

The steric arrangement of the functional groups is not only important for the hydroxybenzoic acids, but also in those cases when more than one hydroxyl group is present in the molecule. Figure 9 shows the adsorption curves of 2,3-, 3,4- and 2,5-dihydroxybenzoic acid. The pH value affects the adsorption densities of the three compounds in three quite distinct ways: In all cases, a rapid increase is observed between pH 4 and 5. However, with increasing pH value, the adsorbed

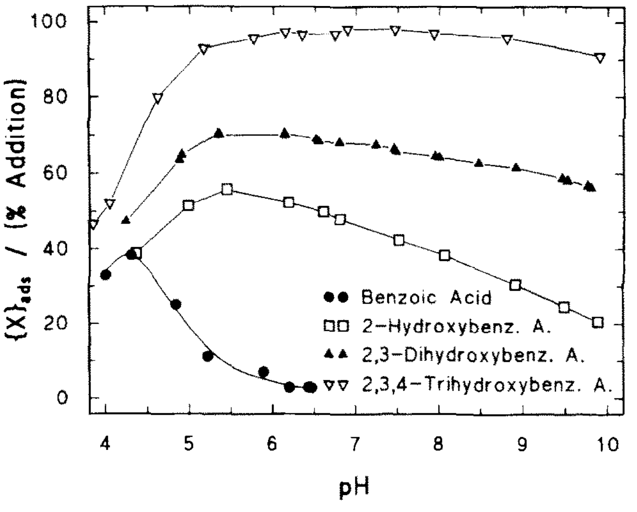


Fig. 7. Adsorption curves of benzoic acid, 2-hydroxy-, 2,3-dihydroxy- and 2,3,4-trihydroxybenzoic acid on α-Al_2O_3.

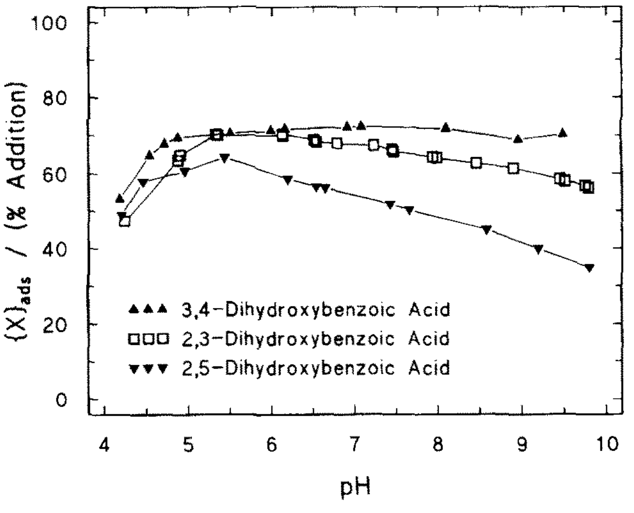


Fig. 9. Adsorption curves of 2,3-, 3,4- and 2,5-dihydroxybenzoic acid on α-Al_2O_3. The lines are intended as a guide to the eyes.

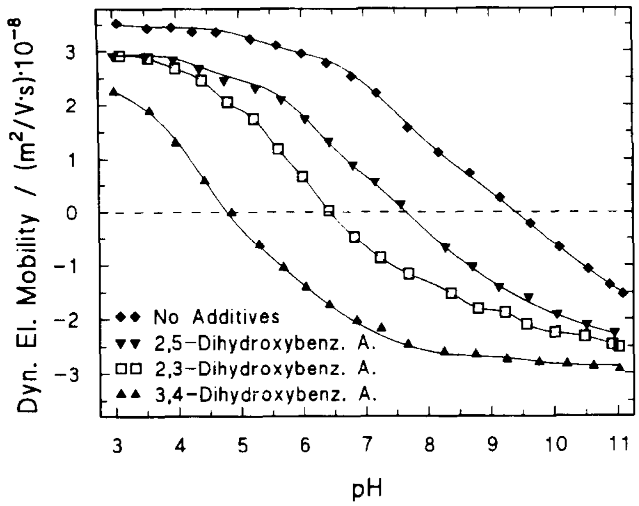


Fig. 10. Influence of 2,3-, 3,4- and 2,5-dihydroxybenzoic acid on the dynamic electrophoretic mobility of alumina particles. The lines are intended as a guide to the eyes.

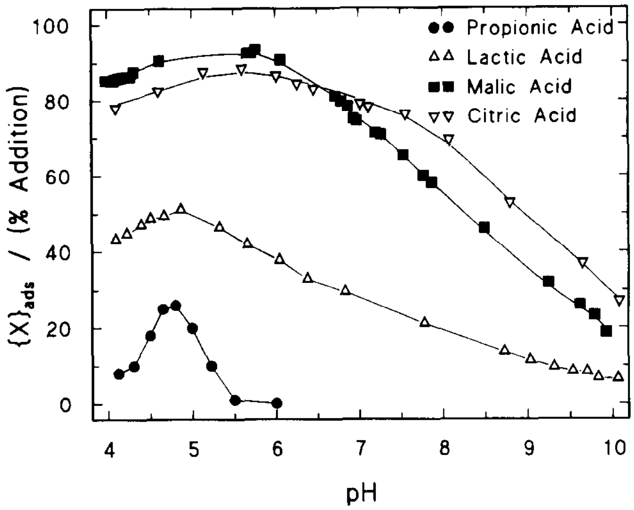


Fig. 12. Influence of propionic, lactic, malic and citric acid on the dynamic electrophoretic mobility of alumina particles. The lines are intended as a guide to the eyes.

amount either remains constant (3,4-dihydroxybenzoic acid), decreases slightly (2,3-dihydroxybenzoic acid), or decreases strongly (2,5-dihydroxybenzoic acid). As expected, these differences are reflected in the influence of the three molecules on the electrophoretic mobility of the alumina particles (Fig. 10). Since the number and the pKa values of the functional groups are the same for all three compounds, these differences are clearly a consequence of different adsorption behaviours.

3.2 Aliphatic compounds

The adsorption curves of propionic, lactic, malic and citric acid are shown in Fig. 11. There are many similarities between the adsorption behaviours of aromatic and aliphatic compounds. Propionic acid, like benzoic acid, has a relatively sharp adsorption maximum in the acidic pH region (pH 4-7). The presence of a hydroxyl group in the α-position (lactic acid) not only results in an increase of the amount adsorbed, but also in an extension of the pH range in which the molecules adsorb onto alumina. The same behaviour was observed in the case of benzoic acid and 2-hydroxybenzoic acid. The presence of a second (malic acid) and third (citric acid) carboxyl group leads to a further increase in the adsorption, mirroring the behaviour of the aromatic compounds.

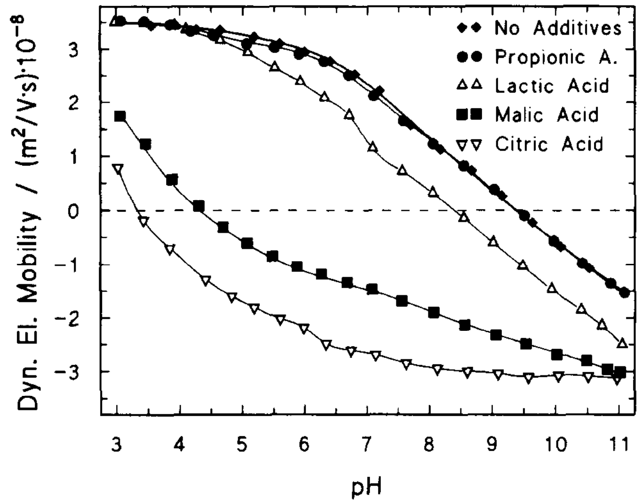


Fig. 11. Adsorption curves of propionic (XIV), lactic (XV), malic (XVI) and citric acid (XVII) on α-Al_2O_3. The lines are intended as a guide to the eyes.

When we compare adsorption data for these molecules with the molecules' influence on the electrophoretic mobility, we find the same trends as have been seen for the aromatic compounds. The shift of the particle charge and the IEP increase both with the adsorption ability and with the number of functional groups (Fig. 12).

3.3 Discussion

The adsorption curves of the hydroxyl- and carboxyl-substituted benzene molecules display one common property: the maximum adsorption density is in the pH range of the pKa values of the dissociable groups. Benzoic acid, for instance, has a pKa value of 4 and an adsorption maximum at pH 4·3, while catechol and pyrogallol with pKa values between 9 and 14 show maximum adsorption densities in the basic pH regime. A similar correlation between the adsorption density and the pKa value of the dissociable groups has also been found for citric acid[9] as well as for other compounds.[22-24] This behaviour can be explained by the ligand-exchange model.[22,25] The oxygen atom of the surface hydroxyl group can act as a donor (Lewis base) and coordinate with protons or metal ions (Lewis acids), whereas the underlying structural Al(III) ion in the surface layer acts as a Lewis acid, which can exchange the (–OH) group for other coordinating anions. Thus, the specific adsorption of an organic molecule on the alumina surface can be described as a ligand-exchange process involving a multi-step reaction sequence.[26]

$$LH^{1-n}(aq) \leftrightarrow L^{n-}(aq)+H^{+}(aq) \quad (3.1)$$

$$AlOH(s)+H^{+}(aq) \leftrightarrow AlOH_2^{+}(s) \quad (3.2)$$

$$AlOH_2^{+}(s)+ L^{n-}(aq) \leftrightarrow AlL^{1-n}(s) + H_2O \quad (3.3)$$

where AlOH(s) is the surface hydroxyl group, L^n the ligand with the valence n and $AlL^{1-n}(s)$ the surface complex. In a first step, the ligand $LH^{1-n}(aq)$ is deprotonated (3.1). Due to the protonation (3.2), the surface hydroxyl group becomes a better leaving group, enabling exchange with the ligand (3.3). In the case of high ligand concentrations or of a high affinity of the ligand to the alumina surface, the intermediate step (the activation of the Al-OH group 3.2) might not be necessary and reaction (3.3) might occur immediately. We note that the adsorption of a ligand does not necessarily lead to a change of the surface charge. According to the ligand-exchange model,[22,25] such an adsorption is a simple exchange of the (OH^-) group for another dissociated group (i.e. $R\text{-}COO^-$) basically without influence on the surface charge. A change of the surface charge can only be achieved (i) if an additional dissociated group, which is not coordinated to the surface, is present in the molecule, (ii) if two dissociated groups coordinate to the same Lewis acid centre or (iii) if an ($-OH_2^+$), which is the better leaving group, is exchanged instead of an (–OH) group.

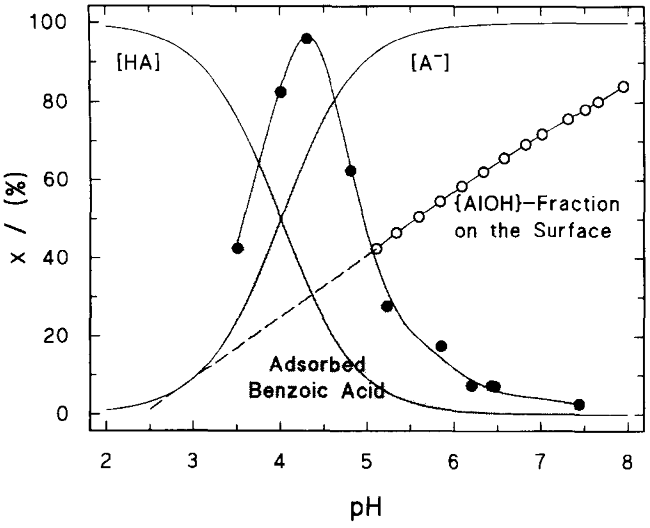


Fig. 13. Relation between the pKa value of the functional group and the adsorption maximum. The values of the benzoic acid adsorption on $\alpha\text{-}Al_2O_3$ have been taken from Fig. 3. For better visibility, they are plotted 2·5 times higher. The speciation of the benzoic acid has been calculated with a pKa value of 4.[31] [HA] and [A^-] are the labels for the protonated and deprotonated species of benzoic acid in solution. The calculation of the percentage Al-OH concentration on the particle surface is based on a total exchange capacity of 2·56 OH groups/nm^2 (Section 2.1). The maximum adsorption occurs at pH 4·3, which is near the pKa value of benzoic acid.

The surface-complex formation of the studied dispersants on alumina and its pH dependence can therefore be rationalised as follows:

(i) If the pH of the suspension is much lower than the pKa value of the ligand ($pH \ll pKa$) the adsorption of the ligand is suppressed by its reaction with a proton.

(ii) If the pH of the suspension is much higher than the pKa value of the ligand ($pH \gg pKa$), the 'reactivity' of the alumina surface will be low because of the small number of protonated surface hydroxyl groups. In addition, the electrostatic interaction between ligand and alumina surface becomes more and more unfavourable. Eventually this interaction can even become repulsive.

(iii) As a result of (i) and (ii), the most favourable conditions for an adsorption exist when the suspension pH is the range of the pKa value of the ligand ($pH \sim pKa$).

If we combine eqns (3·1), (3·2) and (3·3) we can formulate the equilibrium constant *K* for the complex formation:

$$K = \frac{\{AlL^{1-n}\}}{\{AlOH\} \cdot [LH^{1-n}]} \quad (3{\cdot}4)$$

As long as pKa of the ligand is lower than the pH_{ZPC} ($pKa<pH_{ZPC}$), we expect to find maximum adsorption density near the pKa value of the ligand. For this condition the product of the starting compounds is large around the pKa value leading to a high adsorption density. If the pKa value of the ligand is higher than the pH_{ZPC} of the powder, ($pH_{ZPC} < pKa$), the product of the 'starting materials' is highest at the ZPC. Therefore we expect the highest adsorption density to occur near the ZPC of the metal oxide, assuming that the ligand adsorbs at all. Such a constellation can occur for acidic oxide powders such as SiO_2.[16]

Figure 13 illustrates this relation between adsorption density, pKa value of the ligand and ZPC of the powder for the first case. The adsorption curve of benzoic acid on alumina (Fig. 3) is plotted together with the acid-base properties and the concentration of the Al-OH groups on the surface. Figure 13 clearly demonstrates that the best conditions for adsorption of benzoic acid exist around the pKa value. At lower pH values, the concentration of benzoic acid is higher, but the concentration of the Al-OH groups on the surface is too low. At a higher pH, just the opposite is true: the concentration of Al-OH is higher, but the benzoic acid in solution is too low. In cases where a ligand has several dissociable groups of different pKa values, we observe a broad adsorption maximum (Figs 1, 3, 7). In conclusion: by combining functional groups with different pKa values in the same molecule, we get a molecule that shows a high adsorption ability in a wide pH range.

A second important factor for the adsorption ability of a dispersant is the position of the functional groups. One example is the adsorption behaviour of 2-, 3- and 4-hydroxybenzoic acid. Based on the pKa values alone (Table 1), the adsorption of 3- and 4-hydroxybenzoic acid should be favoured over that of 2-hydroxybenzoic acid. However, 2-hydroxybenzoic acid not only shows the highest adsorption density, but also the greatest effect on the electrophoretic mobility. This higher affinity of 2-hydroxybenzoic acid can be explained if we consider the position of the functional groups: The ortho position of the hydroxyl group in 2-hydroxybenzoic acid allows the formation of a chelate complex by coordination of both groups to a surface Al(III) atom. Such a chelate complex including both functional groups is not possible in the case of the 3- and 4-hydroxybenzoic acids. Their adsorption behaviour is mainly governed by the carboxyl group, as can be seen by comparison with benzoic acid adsorption behaviour. Figure 14 shows the proposed structures for the most likely surface complexes that are formed by the adsorption of these three compounds on the alumina surface. The proposed structures for the surface complex of 2-hydroxybenzoic and 4-hydroxybenzoic acid have been confirmed by IR spectroscopy for their adsorption on goethite.[27,28] Biber,[29] who has investigated the adsorption of 2-hydroxybenzoic acid on α-alumina by IR spectroscopy, excludes the participation of the hydroxyl group. However, our results suggest the opposite in light of the different adsorption behaviour of these three molecules.

The steric arrangement of the functional groups also influences the adsorption behaviour of the dihydroxybenzoic acids. At pH 4, the adsorption characteristics of all dihydroxybenzoic acids are very similar and are mainly influenced by the carboxyl group (Fig. 9). At higher pH values, however, differences appear. In 2,5-dihydroxybenzoic acid, the position of the hydroxyl groups on the benzene ring does not allow for a simultaneous coordination of both groups to the alumina surface. This explains the reduced adsorption density, especially in the alkaline pH region. 2,3- and 3,4-Dihydroxybenzoic acid, on the other hand, can form a chelate complex by coordinating to the alumina surface simultaneously with both hydroxyl groups. The slightly higher adsorption density of 3,4-dihydroxybenzoic acid in the alkaline pH region is probably due to the fact that the carboxylate group points away from the alumina surface when both hydroxyl groups are coordinating to the surface. This steric arrangement avoids repulsive electrostatic interactions between the carboxylate group and the alumina surface, which becomes more and more negatively charged with increasing pH. In the case of the 2,3-dihydroxybenzoic acid, the carboxylate group always points in the direction of the alumina surface.

The influence of the electrostatic interaction between the negatively charged ligand and the alumina surface can also be demonstrated in the case of phthalic and hemimellitic acids. At low pH values, the adsorption of hemimellitic acid exceeds that of phthalic acid. At high pH values, however, more phthalate (doubly charged) than hemimellitate (triply charged) is adsorbed on the alumina surface.

The aliphatic compounds follow the same patterns. Propionic acid shows a sharp adsorption maximum near its pKa value. The presence of a hydroxyl group in the α-position (lactic acid) enables the formation of a chelate complex, which not only results in an increase in the amount adsorbed, but also in an increase of surface charge by the additional functional groups. The additional functional groups in malic and citric acid

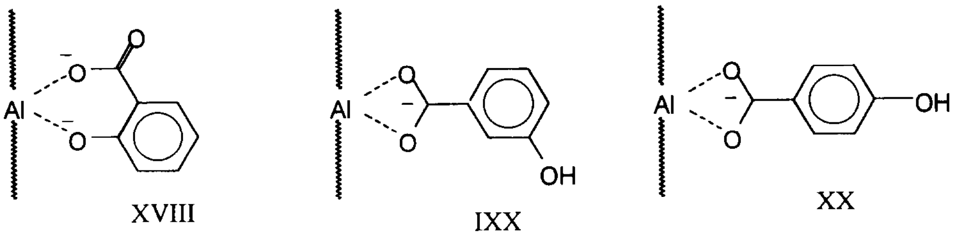


Fig. 14. Suggested structures of the surface complex of 2-, 3- and 4-hydroxybenzoic acid. The proposed structures for the surface complex of 2-hydroxybenzoic and 4-hydroxybenzoic acid have been confirmed by IR-spectroscopy for the adsorption of these molecules on goethite.[27,28]

lead to an even higher adsorption over a broader pH range.

When we compare the impact of the different molecules on the electrophoretic mobility of alumina, which we may regard as an indicator of the change in the surface charge, we observe two trends. First, the change of the surface charge becomes greater with increasing absorption of the molecules, assuming that the number of dissociable functional groups remains constant. Second, in the case of molecules with similar adsorption abilities, the change in the surface charge increases with the number of dissociable groups, as we have seen in the examples of phthalic and hemimellitic acids in the low pH range (Figs 3 and 4).

If we look at the behaviour of the electrophoretic mobility over the entire pH regime, it becomes evident that the influence of the dispersants is stronger in the acidic and neutral pH range, as compared to the alkaline. This is also true for a constant adsorption of the dispersant over the whole pH range. This behaviour is best illustrated by the example of 2,3- and 2,3,4-trihydroxybenzoic acid (Figs 8 and 9). There are two possible explanations for this observation. First, with increasing suspension pH, more and more base must be added to attain the desired pH value. This leads to an increase in the suspension's ionic strength and, as a consequence, to a decrease in the Debye length.[30] Second, the adsorption process amounts to an exchange of a surface ($-OH_2^+$) or ($-OH$) with a dispersant molecule. At low pH values, a protonated ($-OH_2^+$) surface group will be preferentially exchanged with the dispersant. However, with increasing pH and a constant adsorption density, an increasing number of ($-OH$) groups has to be exchanged as the concentration of the ($-OH_2^+$) groups on the surface decreases. The exchange of a ($-OH$) group alone, however, results in no change of the surface charge, as discussed earlier.

4 Summary

The effect of a dispersant with a small molecular weight on the properties of an alumina suspension is determined by (i) its adsorption ability on the particle surface and (ii) the nature and number of its dissociable groups. The following guidelines have been derived by using substituted benzene rings as model compounds. However, they are also applicable to other compounds, as we have demonstrated in the example of aliphatic carboxylic acids.

(1) The adsorption curves of benzene rings that have been substituted with hydroxyl and carboxyl groups are markedly influenced by the number and position of these groups on the ring. The degree of adsorption of a dispersant increases with its ability to form one or more chelate rings with the particle surface. In addition, the degree of adsorption is increased (especially at higher pH values), when groups that are already dissociated point away from the alumina surface, thereby avoiding unfavourable electrostatic interactions.

(2) The pKa value of the dissociable groups of the dispersant and the pH_{ZPC} of the powder particles determine the pH range at which the adsorption maximum occurs. If the pKa value of the ionizable group is lower than the pH_{ZPC}, then the adsorption maximum of a dispersant can be expected in the pH range corresponding to the pKa values of its dissociable groups. In the event that a pKa value is higher than the pH_{ZPC}, the adsorption maximum should occur around the pH_{ZPC}. By combining functional groups with different pKa values in the same molecule, we can get a high degree of adsorption over a wide pH range.

(3) The adsorption process can be described as a ligand exchange, where a surface hydroxyl group is exchanged for another group. A change of the surface charge by the adsorption of a dispersant will therefore only occur (i) if an additional dissociated group that is not coordinated to the surface is present in the molecule, (ii) if two dissociated groups coordinate to the same Lewis acid centre or (iii) if an ($-OH_2^+$), which is a better leaving group, is exchanged instead of an ($-OH$) group.

(4) Assuming similar adsorption densities, the change in surface charge per adsorbed dispersant increases with the number of dissociable groups ('charge carriers') in a molecule.

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