Zeta Potential of Various Oxide Particles and the Charging Mechanism

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2641, Yamazaki, Noda-shi, Chiba 278-8510各種酸化物粒子の ζ 電位と帯電機構

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The charging behavior of various oxide particles was investigated using the zeta potential, which is affected by the electronegativity of the metal ion in an oxide and the properties of the solvents. Acetone, methylethylketone, cyclohexanone, ethanol (EtOH), 1-propanol (1-PrOH) and 1-butanol (1-BuOH) were used for the bath. In the case of the I_2 -added ketone bath, the H^+ ion concentration increased with increasing I_2 content. The zeta potential of the various oxide particles was changed to positive. The zeta potential of the oxides was large in the high H^+ ion concentration bath. Accordingly, the positive charged oxide particles were attributed to the adsorption of H^+ ion onto the particles. In the case of alcohol, included H_2O generates H^+ and OH^- by electrolytic dissociation. Therefore, the zeta potential becomes large in the case when the electronegativity of the metal ion in oxide is low, and the H^+ ion behaves as a potential determining ion.

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1. Introduction

The advantages of the electrophoretic deposition method are: (1) obtaining a uniform and dense coating in a short time, (2) easy control of the thickness and the density of the coating by the deposition voltage and time.¹⁾ Therefore, coatings can be obtained on various shapes and size substrates by this method. Several studies using this method are now being conducted.¹⁾ In this method, oxide particles must be charged in the electrophoretic deposition bath. The charging mechanisms of the particles in an aqueous polar solvent,²⁾ nonaqueous nonpolar solvent²⁾ and nonaqueous polar solvent^{3),4)} have been reported. Generally, the charging magnitude of the oxide is affected by the amount of potential determining ion, dielectric constant of the solvent and ion concentration.²⁾ The charging magnitude is estimated by the zeta potential.

In our previous paper,⁵⁾ it was explained that the charging mechanism was related not only the dielectric constant of the solvent and the potential determining ion concentration but also the adsorption of H^+ ion on the particles and electronegativities of the metal ions in the oxides such as $YBa_2Cu_3O_{7-\delta}$ and $BaTiO_3$.⁵⁾ The solvent was acetone with I_2 in order to generate H^+ ions.

In this paper, we attempted to explain this charging mechanism that is related to the adsorption of H^+ ion as the potential determining ion and the electronegativity of the metal ion in the oxide in various solvents. The solvents used were I_2 -added ketone and alcohol as the protic solvent. These solutions contained a small amount of H_2O because of the electrolytic dissociation.

2. Experimental

The average particle size of the oxide is about $3\mu m$. Reagent grade organic solvents from Wako Pure Chemical Industries, Ltd., Osaka, Japan, were used. The physical properties of the organic solvents are shown in Table 1. These organic solvents were dehydrated using molecular sieves, and the H_2O contents of the organic solvents were measured using a Karl Fisher Moisture Titrator (Kyoto Electric, Inc., MKA-3P). For the determination of the H^+

Table 1. Physical Properties of Organic Solvents^{6),9)}

organic solvents	relative dielectric constant	viscosity (cP)	enol type (%)
acetone	20.7	0.322	1.5×10^{-4}
methylethylketone	18.5	0.441	1.2×10^{-4}
cyclohexanone	18.3	2.453	1.2
ethanol	24.3	1.19	-
1-propanol	20.1	2.20	-
1-butanol	17.5	2.95	-

ions in a bath, a neutralization titration was performed using a 0.01 N NaOH solution after an excess of $Na_2S_2O_3$ was added in order to remove the residual I_2 .⁵⁾ The conductivity of the baths was measured at 25°C using a conductivity meter (TOA Electronics, Ltd.). The zeta potential of an oxide (oxide concentration: 0.01 g/l) was measured at 25°C using an automated electrokinetics analyzer (Pen Kem, System 3000).

3. Results and discussion

3.1 Zeta potential in ketone baths

3.1.1 Zeta potential with the addition of I_2 and H_2O

The acetone molecule generated an H^+ ion through interaction with the additives H_2O and I_2 :

It is assumed that the generated H^+ ion is adsorbed on the surface of the metal oxide particles.⁷⁾ The surface of an oxide has a hydroxyl group due to chemical adsorption. The electrification process is drawn in Fig. 1.⁸⁾ In our previous study, the zeta potentials of the particles in an I_2 -added acetone were positive because of the adsorption of H^+ ion.⁵⁾

Therefore, this mechanism was applied not only to

Surface of oxide particle

Fig. 1. A schematic model for the formation of surface hydroxyl group and the electrification process.⁸⁾

acetone but also to the other ketone containing I_2 in order to generate H^+ ion as in Eq. (2). It is known that the percent of the keto-type and enol-type differs with the ketone as shown in Table 1.⁹⁾ The H^+ ion concentrations increased with increasing concentration of I_2 as shown in Fig. 2. It is concluded that the formation of H^+ ion is based on keto-enol tautomerism like acetone in methylethylketone and cyclohexanone. Experimentally, in the case when the dielectric constant of the solvent is large, the ion is stabilized by solvation and the ion concentration increases. Therefore, the large order of the H^+ ion concentration as a result of reaction between the enol-type ketone and I_2 is the same as that of the dielectric constant.

The adsorption of H^+ ion onto the oxide particle in I_2 -added ketone was then investigated. In Fig. 3, the white marks show the conductivities of the oxide-free baths. The conductivity increased with increasing H^+ ion concentration. The order of the conductivity for the solutions was opposite to that of the H^+ ion concentration. It is considered that acetone has a relatively high dielectric constant and a low viscosity, therefore, the ions easily move in the bath. For the addition of $\alpha-Al_2O_3$ in ketone with I_2 , the conductivity of the baths decreased (Fig. 3). In the case of I_2 -free bath, the conductivity was increased to about 10^{-7} – 10^{-6} S·cm by the addition of $\alpha-Al_2O_3$. It has been assumed that the conductivity of the bath is affected by the decrease in ion concentration due to the adsorption of the ion onto the oxide rather than by the addition of $\alpha-Al_2O_3$. In this case, the zeta potential of oxide may be changed.

Accordingly, the zeta potential of the various oxide particles was measured in the acetone, methylethylketone and cyclohexanone with the different amounts of I_2 (Fig. 4). These solvents contained about 0.13 mol/l H_2O . In the case of the I_2 -free baths, the zeta potential of the various oxide particles is near 0 mV or negative. It is likely that the oxygen on an oxide surface is charged partially ($M(\delta^+)-O(\delta^-)$) and the ion concentration is very low in pure organic solvent. Therefore, the zeta potential of oxide is 0 mV or negative. With the addition of I_2 to the bath, the zeta potential rapidly increased and became positive. It was considered that the H^+ ion generated by the addition of I_2 was adsorbed onto the surface of the oxide particles.

Moreover, the relationship of the zeta potential and the amount of H_2O were measured as shown in Fig. 5. Small amounts of H_2O in organic solvent are needed as a catalyst in Eq. (1). The zeta potential of these oxides increased with a small addition of H_2O . However, by adding more H_2O , the zeta potential decreased. In the case of cyclohexanone, the two phases separated over 0.5 mol/l H_2O . The zeta potential was influenced by the amount of I_2 and H_2O because these are related to the reaction by the formation of H^+ ion (Eqs. (1) and (2)). Generally, if the ion concentra-

Fig. 2. Change of H^+ concentration with the amount of added- I_2 . Δ : in acetone bath, $\blacksquare$: in methylethylketone bath, $\bullet$: in cyclohexanone bath.

Fig. 3. Change of specific conductivity with the amount of added- I_2 . Δ : acetone, $\blacktriangle$: acetone with Al_2O_3 powder (20 g/l), $\square$: methylethylketone, $\blacksquare$: methylethylketone with Al_2O_3 powder (20 g/l), $\circ$: cyclohexanone, $\bullet$: cyclohexanone with Al_2O_3 powder (20 g/l).

Fig. 4. Change of the zeta potential of various oxide powders with the amount of added- I_2 (H_2O : 0.13 mol/l). (a) acetone, (b) methylethylketone, (c) cyclohexanone, oxide powder: 20 g/l, $\circ$: MgO , $\square$: Al_2O_3 , Δ : Cr_2O_3 , ∇ : TiO_2 , $\diamond$: WO_3 .

Fig. 5. Change of the zeta potential of various oxide powders with the amount of added- H_2O (I_2 : 7.88×10^{-4} mol/l). (a) acetone, (b) methylethylketone, (c) cyclohexanone, oxide powder: 20 g/l, $\circ$: MgO , $\square$: Al_2O_3 , $\triangle$: Cr_2O_3 , ∇ : TiO_2 , $\diamond$: WO_3 .

tion is dilute, the H^+ ion is preferentially adsorbed onto the oxide particles.²⁾ Consequently, the zeta potential increased with increasing ion concentration. If the ion concentration is further increased, the zeta potential decreased because of the compression of the electrical double layer.²⁾ The H_2O is needed as a catalyst, however, it seems that the extra amount of H_2O before the phase separation influences the compression of the electrical double layer. Therefore, the zeta potential curve has a maximum as a function of H_2O concentration. In the case of the I_2 and H_2O -added cyclohexanone bath, the amount of H^+ ion adsorbed is higher than that for the other baths. As a result, the order of the zeta potential for various kinds of oxides became acetone < methylethylketone < cyclohexanone as shown in Figs. 4 and 5.

3.1.2 Zeta potential and electronegativity of metal ion in oxide

In Figs. 4 and 5, the zeta potential in the same solvent is different with the kind of oxides. In Fig. 1, H^+ ion is adsorbed on the oxygen in hydroxyl group. This is based on the model of the solid acid-base of an oxide; the basicity of the oxide depends on the electronegativity of the metal ion. Therefore, we investigated the relation between the zeta potential and electronegativity of a metal ion in an oxide. The adsorption of H^+ ion in the solvent affects the partial charge density of oxygen in the hydroxyl group, which is polarized $\text{M}(\delta^+) - \text{O}(\delta^-)$. The adsorbing strength is changed with electronegativity of the metal ion in the oxide. In the case of a low electronegativity of a metal ion, the negative charge density of the oxygen on the oxide surface is large. Therefore, H^+ ion is adsorbed onto the oxide surface and the zeta potential becomes large or changes to positive.

The partial charge density of oxygen on the oxide surface increases with decreasing electronegativity of the metal ion (Fig. 6).¹⁰⁾ Figure 7 shows the relation between the electronegativity of the metal ion and the zeta potential of the oxide in the I_2 -added acetone bath.⁵⁾ The zeta potential of an oxide increased with decreasing electronegativity of the metal ion. Consequently, in the case of the H^+ ion as the potential determining ion, it is considered that the zeta potential of the oxide is influenced by the electronegativity of the metal ion.

3.2 Zeta potential in alcohol baths

In the case of the I_2 -added ketone bath, H^+ ion behaves as the potential determining ion, and the zeta potential is in-

Fig. 6. Relation between a partial charge density of oxygen in the oxide and electronegativity (χ_i) of a metal ion.⁹⁾

Fig. 7. Relation between zeta potential of an oxide in acetone bath (I_2 : 3.94×10^{-3} mol/l) and electronegativity (χ_i) of a metal ion.⁵⁾

fluenced by the electronegativity of the metal ion in the oxide. We investigated the relation between electronegativity and charging mechanism due to the adsorption of H^+ ion in a protic solvent like an alcohol. A small amount of H_2O in the alcohol generated H^+ and OH^- by electrolytic dissociation. In the case of the H^+ ion, it behaves the potential determining ion, and the zeta potential is influenced by adsorption of H^+ ion onto the oxide in organic solvents like an alcohol.

In Fig. 8, the electronegativity of the metal ion in oxides becomes small, and the zeta potential becomes large in EtOH regardless of the H_2O content being the same as in Fig. 7.

Figure 9 shows the relation between the zeta potential in several alcohols and the electronegativity of the metal ion. As the electronegativity of the metal ion in the oxides becomes small, the zeta potential becomes large regardless of the alcohol. The order of the zeta potential in solvents is $1\text{-BuOH} > 1\text{-PrOH} > \text{EtOH}$. This order is the same as the value of the relative dielectric constant (Table 1).⁶⁾ It has been assumed that the H^+ ion tends to adsorb on the oxide in the relatively small dielectric constant bath, because the H^+ ion is difficult to exist in the solvent. Moreover, it is necessary to study in the future the dissociation of H^+ ion

Fig. 8. Relation between zeta potential of oxide particles and electronegativity (χ_i) of a metal ion in ethanol bath. H_2O : (a) 5.56×10^{-1} , (b) 1.67×10^{-1} , (c) 2.13×10^{-2} , (d) 1.41×10^{-2} mol/l.

Fig. 9. Relation between zeta potential of oxide particles and electronegativity (χ_i) of a metal ion. H_2O : 2.13×10^{-2} mol/l, (a) EtOH, (b) 1-PrOH, (c) 1-BuOH, oxide powder: 20 g/l.

from alcohol.

As a result, in the case of the H^+ ion, it behaved as the potential determining ion in alcohols, and it has been assumed that the determination of the zeta potential is affected by the electronegativity of the metal ion and dielectric constant of solvent. These results are similar to that of the I_2 -added ketone baths.

4. Conclusions

The charging behavior and the zeta potential of various oxide particles were investigated in various I_2 -added ketone baths and EtOH, 1-PrOH and 1-BuOH. In the I_2 -added ketone baths, as the percent of the enol-type increases, H^+ ion concentration increases. If the electronegativity of the metal ion in oxides is lower, the zeta potential becomes large. The order of the zeta potential is cyclohexanone > methylethylketone > acetone; this order is the same as the amount of H^+ ion adsorbed. In protic solvents such as EtOH, 1-PrOH and 1-BuOH, the electronegativity of the metal ion in oxides is lower, and the zeta potential also becomes larger. The zeta potential of the oxides in these alcohols depends on the dielectric constant of the solvents and the H_2O concentration in the baths. In conclusion, H^+ ion behaves as a potential determining ion, and the zeta potential is changed by the amount of H^+ ion adsorbed on the oxide surface, which is influenced by the electronegativity of the metal ion.

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