Surface charge and coagulation of aqueous ZnO dispersions

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Surface Charge and Coagulation of Aqueous ZnO Dispersions

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Different pretreatments of ZnO lead to differences in surface carbonate groups and in interstitial Zn content, while the ζ potential is determined only by the concentrations in the electrolyte solution. The rate of coagulation however, is determined by the ζ potential, independent of the way in which this is arrived at. The surface charge of ZnO cannot be described by the site-binding model; rather, mutual stimulation of the adsorption of H^+ and chemisorption of anions is indicated. © 1986 Academic Press, Inc.

INTRODUCTION

ZnO has been the subject of extended colloid chemical investigations (see, e.g., Refs. (1–5)). One of the interesting aspects of ZnO from a colloid chemical point of view is, that one ζ potential can be found combined with different situations at the ZnO/aqueous solution phase boundary (different amounts of adsorbed ions, or of interstitial Zn). Thus, ZnO can be used to check whether the interaction between suspended particles is noticeably affected by changes of such parameters.

ZnO preparations normally have hydroxyl and carbonate groups on their surface (6) but these can be removed by heating. Such surface groups might influence coagulation through changing the adsorption of ions or the dissolution of Zn^{2+} -containing complexes. Thus, Healy and Jellett (1) postulated that coagulation be enhanced by the presence of uncharged polymeric $Zn(OH)_2$ complexes in the solution. However, when removing adsorbed impurities from the ZnO surface, e.g., by heating, other properties of the solid are effected as well, such as the degree of disorder near the phase boundary; the number of electron donors, etc.

The present investigation aims at elucidating the question whether the coagulation rate of ZnO is determined once the ζ potential has been fixed, or whether other properties of the

ZnO/aqueous electrolyte solution interface influence either attraction or repulsion.

EXPERIMENTAL

Materials

Merck "Pro Analyti" samples were used throughout, both for the electrolytes employed (KCl, KNO_3 , KI) and for the ZnO used as starting substance (designated as ZnO a.r.). Occasionally, ZnO Highways Ultrapur was employed for comparison.

ZnO was pretreated by heating in a flow of O_2 or N_2 at atmospheric pressure for 4 h at 723 K; these samples are indicated as ZnO/ O_2 and ZnO/ N_2 , respectively, in order to distinguish them from ZnO "as received" (ZnO a.r.).

Treatment of ZnO with H_2 for 4 h resulted in pronounced sintering, which precluded adsorption and coagulation measurements.

Therefore pretreatment of ZnO in a reducing atmosphere was performed by heating the sample first for 4 h in oxygen at 723 K; then N_2 was passed through for 15 min; thereafter H_2 was passed through and the oven was turned off. The sample was then cooled under a flow of hydrogen. Such samples are indicated as ZnO/ H_2 .

For further experiments the samples were directly transferred from the ignition tube to

the apparatus. In some series of experiments, the heating temperature was varied.

Ellipsometry measurements were performed on a ZnO single crystal, kindly provided by Prof. Heiland (Aachen, GFR)¹; it had been grown from the vapor phase.

Characterization of the ZnO

ESR measurements showed, in agreement with Iyengar and Codell (7), a decrease of the signal at $g = 1.965$ on heating in O_2 , while this signal increased on heating in He and especially so on heating in H_2 . This signal is attributed to interstitial Zn (7); its ratio, in the direction $ZnO/O_2:ZnO \text{ a.r.}:ZnO/He:ZnO/H_2$, is about 1:3:10:50.

The signal at $g = 2.003$, ascribed to O^- , increases in a similar way to the 1.965 signal by heating in He or H_2 , but is not changed significantly by heating in O_2 .

Interstitial Zn, as determined by Norman's method (8), amounts to 6.3 ppm in ZnO/O_2 ; 8.5 ppm in $ZnO \text{ a.r.}$; 6.0 ppm in ZnO/N_2 ; and 74.9 ppm in ZnO/H_2 .

The amount of surface hydroxyl groups, determined by Morimoto and Naono's method (9), is 8.3–9.5 OH groups/nm² irrespective of pretreatment. The possibility cannot be excluded that the ZnO is covered by OH groups during the transfer from the ignition tube to the analytic apparatus; but then the same effect should be expected for the ZnO used in surface charge, electrokinetic and coagulation experiments.

Surface carbonate groups were determined in the same apparatus as used for OH group determination, with 1 M HCl solution replacing the methyl magnesium iodide reagent in the latter. ZnO a.r. contained 1.95 groups/nm²; heat-treated ZnO: 0 ± 0.3 groups/nm², irrespective of the atmosphere during heating. The carbonate groups disappeared at 473–493 K, in agreement with Morimoto and Morishige's data (6).

The surface area of heat-treated ZnO, measured by nitrogen adsorption, amounted to 3.5 m² g⁻¹.

EXPERIMENTAL PROCEDURES

Electrokinetic and coagulation rate measurements were performed in dilute suspensions (3.2 mg in 25 ml), prepared as described previously (10). Adjustment of the pH in the initial suspension was much more rapid for preheated ZnO than for ZnO a.r.: for the preheated ZnO only one major pH correction and one dispersion procedure were necessary for obtaining a stable pH.

The initial coagulation rate was calculated from E (= light extinction) versus t (= time) graphs, through $(dE/dt)_{t=0}/E_0^2$; $E_0 = E$ at $t = 0$. The philosophy for so doing is, that the coagulation rate is proportional to n^2 (n = the number of particles), while E_0 is proportional to n_0 . Thus a comparison of the initial coagulation rate for suspensions with slightly varying solid concentrations is achieved. Only relative coagulation rates are presented in the present paper.

Surface charge measurements were performed in concentrated suspensions (7.00 g ZnO in 300 ml) by the pH stat method described by Trimbos *et al.* (5). The liquid phase was, before addition of the ZnO, saturated by 15 mg of ZnO; the attainment of solubility equilibrium was followed through the accompanying H^+ or OH^- consumption. Solubility equilibrium was established in 0.5–15 h, depending on the pH; additional small ZnO doses did not have any effect. After saturation of the liquid, 7.00 g of ZnO was added directly from the ignition tube.

A subsequent net OH^- consumption is indicated as $\Gamma_{OH^--H^+}$ ($\mu M \cdot m^{-2}$); it is negative when a net amount of H^+ was consumed. All surface charge measurements were performed in the dark.

In some cases, fast titrations were carried out in the same apparatus as used for $\Gamma_{OH^--H^+}$ determination, by the method described in Ref. (5).

¹ The authors express their gratitude to Professor Heiland for placing the crystal at their disposal.

Ellipsometry was performed on a ZnO single crystal ($0.5 \cdot 0.4 \cdot 0.1 \text{ cm}^3$) embedded in a resin ("transparent resin No. 3", Struers) by applying a pressure of about 10^7 Pa at 403 K . The 0001 crystal face was polished successively with 3-, 1-, and $0.25\text{-}\mu\text{m}$ diamond powder, and rinsed with 76% ethanol; after drying in hot air, the crystal was stored over CaCl_2 .

The ellipsometer used was a Rudolph automatic RR 2000 apparatus. Before measurements, the reflectivity of the crystal was checked in air, and then the crystal was immersed in a 0.01 M KCl solution in a thermostated vessel, under a flow of nitrogen. The pH was varied between 7 and 11. The ellipsometric angles Δ and ψ (11) were registered as a function of time.

RESULTS AND DISCUSSION

1. Ellipsometry

No changes of the ellipsometric angles were found for up to 2 days at $\text{pH} = 9.00$; neither were changes detected at other pH values. (Here measurements were restricted to 5 min per pH value.)

From this negative result, we conclude that no layer characterized by a separate refractive index and extinction coefficient is formed at the ZnO/aqueous electrolyte solution interface. Thus, no $\text{Zn}(\text{OH})_2$ formation other than covering of the ZnO surface by OH groups occurs. The negative result of the ellipsometry measurements is a strong argument against the formation of a porous gel layer on the ZnO surface (12, 13), although a "layer" of subnanometer thickness cannot rigorously be excluded.

2. Measurements of $\Gamma_{\text{OH}^- - \text{H}^+}$

The $\Gamma_{\text{OH}^- - \text{H}^+}$ measurements for ZnO a.r. show the same characteristics as reported by Trimbois *et al.* (5), which had been found by other investigators as well (2, 3). Thus, a fast H^+ or OH^- consumption was followed by a slow process.

This slow process could be suppressed by preheating. Figure 1 shows typical results ob-

FIG. 1. Net consumption of H^+ or OH^- in 10^{-2} M KCl at $\text{pH} = 10.00$ as a function of time for samples of ZnO, ignited in an atmosphere of oxygen at different temperatures (parameter of the curves) for 4 h.

tained for ZnO samples pretreated in oxygen at various temperatures, at $\text{pH} = 10.00$. Especially remarkable is that the slow process disappears at the same preheating temperature ($473\text{--}493 \text{ K}$) where, in agreement with Morimoto and Morishige (6), expulsion of the chemisorbed CO_2 from the ZnO surface was found. The suppression of the slow process was found for ZnO Highways Ultrapur at the same temperature, and the same phenomena were observed for ZnO/O_2 , ZnO/N_2 , and ZnO/H_2 .

Heat treatments in oxidizing and in reducing atmospheres, though effecting pronounced changes in the interstitial Zn content, did not lead to differences in $\Gamma_{\text{OH}^- - \text{H}^+}$ (see Figs. 2 and 3), at least not in the present experiments performed in the dark.

Thus, we must conclude that this slow process is connected with surface carbonate groups rather than with a surface reaction involving ZnOH groups with mobile charge carriers, as suggested earlier by the kinetics of the process (5). Similarly slow H^+ or OH^- consumption as found for ZnO a.r. was found using solid NaHCO_3 or a basic zinc carbonate.

Experiments in 10^{-3} M KCl solutions show

FIG. 2. Net consumption of H^+ or OH^- , on addition of 7.00 g ZnO/O_2 to 300 ml KCl solution, as a function of pH: $\square$ 10^{-3} M; $\times$ 10^{-2} M; $\circ$ 10^{-1} M.

a pronounced peak in the adsorption curve at $pH = 8.55$. Similar though slightly different phenomena were observed in 10^{-3} M KNO_3 solutions (Fig. 4). Such peaks were not found on fast titrations: $\Gamma_{OH^- - H^+}$ as measured by fast titrations follows the course expected in the absence of a peak.

This is illustrated in Fig. 5. Here data obtained by the pH stat method are compared with data obtained on fast titrations: On adding ZnO to the electrolyte solution (which had been previously saturated towards ZnO), first the pH stat value for $\Gamma_{OH^- - H^+}$ was recorded. Afterwards fast titrations were carried out in the same suspensions, as follows:

(a) The titration was started at an initial $pH = 9.00$ to $pH = 8.30$ and back (lower dotted curve in Fig. 5);

FIG. 3. As Fig. 2, for ZnO/H_2 .

FIG. 4. Net consumption of H^+ or OH^- , on addition of 7.00 g ZnO/O_2 to 300 ml KNO_3 solution, as a function of pH: $\square$ 10^{-3} M; $\times$ 10^{-2} M; $\circ$ 10^{-1} M.

(b) The titration was started at an initial pH = 8.55, to pH = 9.00, then back to pH = 8.30 and afterwards up to pH = 8.55 again (upper dotted curve in Fig. 5).

The dotted curves correspond in all cases to the sum of the $\Gamma_{\text{OH}^- - \text{H}^+}$ values obtained during ZnO addition, and during the fast titration. Similar phenomena were observed in 10^{-3} M KNO_3 solutions.

If the 7.00 g ZnO in a pH stat experiment was added in two successive portions of 3.50 g each, with an interval of either 10 min or 24 h, only the first portion showed the peak value of $\Gamma_{\text{OH}^- - \text{H}^+}$; while at other pH values for both portions the same $\Gamma_{\text{OH}^- - \text{H}^+}$ (in $\mu\text{M}/\text{m}^2$) was found on addition of 7.00 g ZnO.

Thus, for interpreting the $\Gamma_{\text{OH}^- - \text{H}^+}$ peaks, we have the following data:

(1) The peaks are related to the first addition of a substantial amount of ZnO; they are observed neither on addition of the 15 mg of ZnO necessary for previous saturation of the solution, nor an addition of a second portion, nor during titration of the suspension after ZnO addition;

FIG. 5. Comparison of pH stat data ($\square - \square$) with fast titration (---) for ZnO/O₂ in 10^{-3} M KCl .

(2) The peaks are influenced by the type of anion present (compare Figs. 2 and 4), but the peaks disappear at higher electrolyte concentration;

(3) The peaks are found both for ZnO/O₂ and for ZnO/H₂ (compare Figs. 2 and 3).

The first effect marks the peaks as being due to impurities rather than to properties of the ZnO itself. But the restriction to the first substantial amount of ZnO added excludes as causes: traces of CO₂ left on the ZnO during the pretreatment; impurities desorbing from the glass vessel; ion exchange of an anionic impurity on the ZnO surface with OH⁻ from the electrolyte solution, and adsorption of OH⁻ on cationic impurities on the ZnO surface. The third effect excludes impurities from the gases used for pretreatment, and interstitial Zn as causes for the peak adsorption; the disappearance at higher electrolyte concentrations excludes impurities from the supporting electrolyte.

An explanation for the phenomena of the peaks is that the ZnO employed contains cationic impurities forming complexes both with OH⁻ and with anions from the supporting electrolyte in a restricted pH range, leading to saturation after addition of the first substantial amount of ZnO. The differences between $\Gamma_{\text{OH}^- - \text{H}^+}$ observed during pH stat experiments and during fast titrations indicate that complexes once formed do not react any more with H⁺ or OH⁻.

We have dealt rather extensively with these peaks, although they are related to impurities, because similar phenomena might complicate adsorption data obtained by the pH stat method for other oxides as well; such data should always be supplemented by fast titrations.

3. The Effect of Anions on $\Gamma_{\text{OH}^- - \text{H}^+}$

Figures 6 and 7 show the dependence of $\Gamma_{\text{OH}^- - \text{H}^+}$ on increasing electrolyte concentration. Quite generally, $\Gamma_{\text{OH}^- - \text{H}^+}$ shifts toward more positive values with increasing electro-

FIG. 6. Net consumption of H^+ or OH^- for additions of 7.00 g ZnO/O_2 to 300 ml KCl solutions as a function of pCl : $\circ$ pH = 10; $\times$ pH = 9; $\square$ pH = 8.

lyte concentration, but does so differently for KCl and for KNO_3 . The value in Fig. 7 for pH = 8 in $10^{-3} M KNO_3$ solution is connected with a "peak," and thus influenced by impurities in the ZnO.

The data are consistent with the hypothesis that anions from the supporting electrolyte are chemisorbed by the ZnO and stimulate the adsorption of H^+ (and/or hinder the adsorption of OH^-).

4. Electrokinetic Measurements

Figure 8 shows the ζ potential vs the pH for ZnO/O_2 in $10^{-2} M$ KCl solutions. Five series of measurements are shown; each series comprises a number of ζ potential measurements at different pH values, performed on one sam-

FIG. 7. As Fig. 6 in KNO_3 solutions: $\blacktriangle$ pH = 8.5.

ple of ZnO/O_2 . Comparison with data for ZnO a.r. (10) shows that heating in oxygen results in pronounced (and not quite reproducible)

FIG. 8. ζ potential as a function of pH for ZnO/O_2 in $10^{-2} M$ KCl. Results of five series.

shifts of the ζ (pH) curve. Notwithstanding the differences between curves obtained on different ZnO/O₂ samples, the curves show similar characteristics: ζ remains negative for $7.8 < \text{pH} < 10$, and the absolute value of the ζ potential shows a minimum (though this is rather shallow for two samples). The reproducibility of the ζ potential measurements for ZnO a.r., ZnO/H₂, and ZnO/N₂ was far more satisfactory. The characteristic turn of the ζ potential to more negative values with decreasing pH will be called an "inversion" of the ζ (pH) curve.

The same type of curve is found for ZnO/H₂ in $10^{-2} M$ KCl solutions (Fig. 9), but in KNO₃ or KI solutions different phenomena are observed (see Figs. 10 and 11, respectively). The final turning (at relatively low pH values) towards positive ζ potential values, found for KNO₃, is to be expected in KCl and KI solutions as well, although at lower pH values than comprised in the present investigation. With KNO₃ solutions, the inversion of the ζ (pH) curve is restricted to a rather narrow pH range and thus might easily escape detection on scanning the pH range.

Such an inversion in the ζ (pH) curve has

FIG. 9. ζ potential as a function of pH for ZnO/H₂ in $10^{-2} M$ KCl. Results of three series.

FIG. 10. ζ potential as a function of pH for ZnO/O₂ in $10^{-2} M$ KNO₃. Results of two series.

FIG. 11. ζ potential as a function of pH for ZnO/O₂ in $10^{-2} M$ KI. Results of two series.

been reported previously by Healy and Jellet (1) and by Trimbos and Stein (5) though not by Nechaev and Shein (14) nor by Ray c.s. (15). The reason for this discrepancy is not clear, too little data being provided by the latter two groups on the ZnO samples.

The ζ (pH) inversion can be understood as follows: At high pH values, ζ is strongly negative; the charge behind the electrokinetic slipping plane here consists predominantly of dissociated surface hydroxyl groups (ZnO^-) which are only partially compensated by adsorbed cations. With decreasing pH, this charge decreases; but simultaneously anions from the supporting electrolyte are chemisorbed to an increasing extent because they experience less repulsion. This in turn leads to an increased adsorption of H^+ ions, as evidenced by the effect of increasing electrolyte content on $\Gamma_{\text{OH}^- \rightarrow \text{H}^+}$ (Figs. 6 and 7).

In a certain pH range the increasing anion chemisorption appears to predominate the effect of increasing H^+ adsorption (or decreasing ZnOH dissociation) on the ζ potential: in this

FIG. 12. Surface charge as a function of ζ potential (ZnO/O_2 in $10^{-2} M$ KCl). The figures near the arrows indicate pH values.

FIG. 13. As Fig. 12, in $10^{-2} M$ KNO_3 .

pH range the ζ (pH) inversion occurs. However, when the energetically most favorable sites for anion chemisorption become more and more occupied, the predominance of increasing anion chemisorption over increasing H^+ adsorption with decreasing pH ceases. Then the net charge behind the electrokinetic slipping plane (σ_ζ) turns toward more positive values.

In the range of compositions and pH values scanned in the present investigation, the turning point towards more positive σ_ζ values has been reached only for KNO_3 solutions.

In the Figs. 12 and 13, we have illustrated this mechanism by plotting the surface charge σ_0 against ζ . Figure 12 relates to one set of data for ZnO/O_2 in $10^{-2} M$ KCl (cf. Fig. 8); the other sets showed the same behavior.

It is seen that, when σ_0 becomes more positive than a certain value ($2.8 \mu\text{C} \cdot \text{cm}^{-2}$ in KCl solutions, $1.4 \mu\text{C} \cdot \text{cm}^{-2}$ in KNO_3 solutions), the ζ potential and consequently the net charge behind the electrokinetic slipping plane become more negative with increasing positive σ_0 values.

This fact is not compatible with the site binding model (16, 17), where Cl^- or NO_3^- ions can be adsorbed only on ZnOH_2^+ sites leading

to $\text{ZnOH}_2^+\text{Cl}^-$ and $\text{ZnOH}_2^+\text{NO}_3^-$ groups, respectively. Our results are compatible with the view that, while H^+ adsorption is simulated by chemisorbed anions (cf. Figs. 6 and 7), the chemisorption of anions in turn is stimulated by H^+ adsorption, being determined by the local rather than by the average potential (5, 18).

The possibility cannot be excluded that the ζ (pH) inversion is connected with impurities in the ZnO; it occurs in the pH range where peaks due to impurities are found in the $\Gamma_{\text{OH}^--\text{H}^+}$ vs. pH curves, though at lower electrolyte concentrations. Nevertheless, it is remarkable that the negative charges behind the electrokinetic slipping plane in this pH region are not compensated either by additional H^+ adsorption or by desorption of anions.

5. Coagulation Rate

In view of the uncertainties in the collision frequencies (10) we will restrain here from a comparison between the coagulation rates observed and those expected from theory; in the context of the present paper especially comparisons between the coagulation rates shown

FIG. 14. Coagulation rate as a function of ζ potential (ZnO/O_2 in $10^{-2} M$ KCl). Results of five series (compare Fig. 9).

FIG. 15. Coagulation rate as a function of ζ potential (ZnO/O_2 in $10^{-2} M$ KNO_3). Results of two series.

by ZnO/O_2 and ZnO/H_2 in different environments are of interest.

Figures 14–16 present data for the coagulation rate of ZnO/O_2 at $10^{-2} M$ KCl, KNO_3 , and KI solutions, respectively. In spite of differences in ζ (pH) curves for various samples of ZnO/O_2 , of the fact that one ζ potential value can be accompanied by quite different values of $\Gamma_{\text{OH}^--\text{H}^+}$, and of differences in ζ (pH)

FIG. 16. Coagulation rate as a function of ζ potential (ZnO/O_2 in $10^{-2} M$ KI). Results of two series.

between different electrolytes, the coagulation rate is determined by the ζ potential value only.

Neither does variation in the atmosphere during heating result in pronounced changes in coagulation rate (Fig. 17). Even the question whether ZnO is preheated or not does not appear in distinct differences in coagulation rate.

Thus, the interaction between ZnO particles can be described by the same attraction irrespective of the amount of interstitial Zn and the presence of carbonate groups on the surface, while the repulsion is determined once the ζ potential has been fixed.

CONCLUSION

The present study leads to the conclusion, that both chemisorption and Hamaker constant are insensitive toward changes in pretreatment conditions and thus to differences in interstitial Zn concentrations.

The insensitivity of chemisorption towards changes in interstitial Zn concentrations is evidenced by the absence of a difference in PZC shift between ZnO/O₂ and ZnO/H₂ on going from 10^{-2} M KCl to 10^{-3} M KCl (see Figs. 2

and 3); the insensitivity of the Hamaker constant is shown by the absence of a difference in coagulation rate between ZnO/O₂ and ZnO/H₂, once the ζ potential has been fixed (see the Figs. 14–17).

This conclusion may come as a surprise. Changes in interstitial Zn in ZnO are expected to lead to changes in surface conductivity in the solid, because interstitial Zn can act as a donor in ZnO. Chemisorption of ions could be expected to depend on surface conductivity because the latter influences the potential changes induced by an ion in its vicinity. The Hamaker constant, on the other hand, is related to the polarizability of the material forming the disperse phase, and an interstitial Zn atom will have a considerably larger polarizability than Zn²⁺ or O²⁻ at lattice sites. Nevertheless, the results of the present study do not leave any doubt with regard to the conclusion mentioned.

An explanation of this result is that the interstitial Zn concentrations reached by the reducing conditions during pretreatment remain too low to influence chemisorption and Hamaker constant.

SUMMARY

Adsorption measurements, coagulation data, and measurements of ζ potential in the ZnO–aqueous electrolyte system have been presented. The mechanism of adsorption and the rate of coagulation are not significantly influenced by the changes in solid-state properties of ZnO. The rate of coagulation of ZnO is fully determined by the ζ potential value.

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