Relationship between Zero Point of Charge and Solubility Product for Hydroxides of Polyvalent Cations

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Abstract □ The zero point of charge (ZPC) of slightly soluble compounds is the pH at which their particles suspended in water have zero charge. The ZPC values of slightly soluble hydroxides were compared with their solubility product in the form of its negative logarithm, pK_{SP}, and with the pH of their suspensions in pure water, pH_{SP}, which is a function of pK_{SP}. The ZPC–pK_{SP} relation was nonlinear while the ZPC–pH_{SP} relation was linear. Either equation can be used to estimate the ZPC value of a hydroxide from its solubility product. The ZPC of a given hydroxide was higher than its pH_{SP} because polyvalent cations are more extensively adsorbed and less extensively desorbed from the particle surface than the monovalent hydroxide ion. At the pH_{SP}, there are equivalent amounts of the cation and of the hydroxide anion in solution, but the surface layer of the hydroxide particle contains an excess cation on an equivalent basis. This imbalance confers a positive charge to the particle. The solubility product of aluminum hydroxide, redetermined at 25° by means of pH measurements, was 8×10^{-33}. Its ZPC, redetermined by microelectrophoresis, was 8.5 ± 0.1.

Keyphrases □ Zero point of charge—slightly soluble hydroxides, related to solubility product □ Solubility product—slightly soluble hydroxides, related to zero point of charge □ Hydroxides, slightly soluble—zero point of charge related to solubility product □ Aluminum hydroxide—zero point of charge related to solubility product

A slightly soluble hydroxide, $M^{z+}(OH)_z{}^-$, of cation M of valence z has a surface layer of composition $[M^{z+}(OH)_n]^{z-n}$, which depends on the pH of the solution. The surface charge of the particle is negative at high pH values where $z < n$ and positive at low pH values where $z > n$. At an intermediate pH value where $z = n$, the surface layer has the same composition as the bulk of the hydroxide particle, and the net charge is zero. This pH value, called the zero point of charge (ZPC) (1–3), is analogous to the isoelectric point of proteins.

The net surface charges at other pH values arise from one of two effects:

1. Frequently, the amphoteric dissociation of surface hydroxide groups produces such a surface charge. For aluminum hydroxide, $Al(OH)_2{}^+$ or $Al(OH)_2OH_2{}^+$ surface groups confer a positive charge to the particle at pH values below the ZPC while $Al(OH)_4{}^-$ surface groups confer a negative charge to the particle at pH values above the ZPC (2, 3).

2. The adsorption from solution of metal hydroxo complexes produced by hydrolysis of material dissolved from the precipitated hydroxide may confer a charge to the particle surface. For aluminum, such complexes include $[Al_8(OH)_{20}]^{4+}$ (4).

BACKGROUND

The ZPC is an important property of the hydroxides. It is equal to the pH value at which their suspensions are most highly flocculated, as shown by maxima in the sedimentation volume, the rate of sedimentation, and the viscosity (2, 5, 6). Since the ζ-potential of the particles at the ZPC is zero, there is no electrostatic repulsion to oppose the interparticle attraction due to London–van der Waals forces. Hence, the most extensive aggregation occurs at the ZPC. An implication of pharmaceutical interest is that caking in aluminum hydroxide and magnesium hydroxide suspensions is least extensive at the ZPC.

The methods used for measuring the ZPC are lengthy and require special experimental precautions (1, 2). In electrokinetic measurements, for instance, supporting electrolytes are used to adjust the ionic strength. These must be indifferent; *i.e.*, the added counterions should display no specific adsorption or interaction with the precipitated hydroxides. If any anions or cations introduced *via* the reagents used in precipitating the hydroxides are adsorbed by the particles, they should be removed. This removal may be difficult because the gelatinous precipitates exhibit pronounced sorptive properties due to their large specific surface areas. Moreover, impurities that may have been incorporated in the bulk of the particles *via* coprecipitation are known to affect the ZPC. These experimental difficulties are reflected by the lack of agreement frequently found among ZPC values reported for a single compound (1).

Solubility products of slightly soluble hydroxides are relatively easy to determine, and an extensive tabulation has been published (7). Values reported for the solubility product of a single compound at a given temperature are generally in good agreement, except for some values published before the late 1930's when reliable techniques for measuring hydrogen-ion activity and concentrations of trace amounts of metals were not available.

Among the published solubility product values, only the value of aluminum hydroxide has some uncertainty attached to it. Reference 7 lists 14 values measured at room temperature; 10 are in the range of 10^{-32}–10^{-30} while the earliest four values, determined in 1924 and 1933, vary between 10^{-17} and 10^{-13}. However, the most recent edition of a widely used handbook lists the following three values: 4×10^{-13} at 15°, 1.1×10^{-15} at 18°, and 3.7×10^{-15} at 25° (8).

In addition to being at variance with the recent values of Ref. 7, this set also seems to be internally inconsistent. When the three values are used to calculate the pH of an aluminum hydroxide suspension at the three temperatures, using the appropriate values for the ionization product of water, the results are 11.37, 10.62, and 10.51, respectively. It is unlikely that the 3° temperature increase from 15 to 18° lowered the pH by 0.75 unit while the 7° increase from 18 to 25° lowered it by only 0.11 unit.

The purpose of this study was to investigate the existence of a correlation between the ZPC of polyvalent hydroxides and the solubility product or the pH value calculated from the solubility product, pH_{SP}. The latter is the pH of a suspension or saturated solution of the hydroxide in pure water. It equals the ZPC only if the surface layer has the same composition as the bulk of the hydroxide particle, e.g., $Al(OH)_3$ in the case of aluminum hydroxide. This condition precludes the adsorption of dissolved hydroxo complexes as well as the amphoteric dissociation of surface groups.

The only measurements made to supplement the published data were redeterminations of the solubility product and of the zero point of charge of aluminum hydroxide for the following reasons. Aluminum hydroxide suspensions are widely used as antacids and as adsorbents for vaccines and toxoids. There are discrepancies in the published values of its solubility product. The published ZPC values differ somewhat among each other and from the values calculated by Eqs. 2 and 3. The redetermined ZPC value of aluminum hydroxide would serve as a verification of these equations.

EXPERIMENTAL

All chemicals were ACS reagent grade. To determine the solubility product of aluminum hydroxide, aluminum sulfate octadecahydrate was recrystallized three times from water. A 0.01 M solution was treated with the stoichiometric amount of sodium hydroxide at the boiling point. The precipitate was immediately purified by washing, electrodialysis, and electrodecantation. It was resuspended in freshly redistilled conductivity water under careful exclusion of carbon dioxide.

The pH of the suspension was measured at $25.0 \pm 0.1°$ at regular intervals, using three different types of pH meters equipped with glass electrode systems. The electrodes were immersed in the upper portion
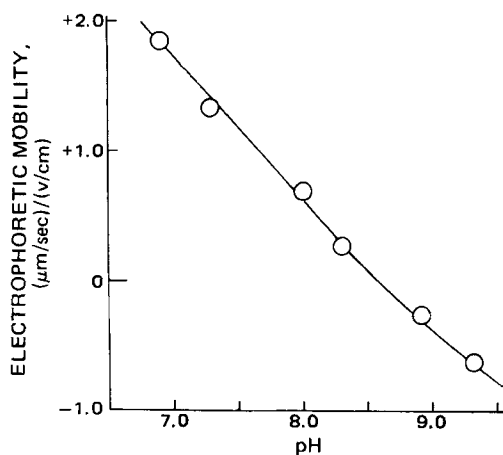
Figure 1—*Effect of pH on electrophoretic mobility of aluminum hydroxide at constant ionic strength.*

of a suspension, and measurements were made after the flocs had settled at least 2 cm below the electrode tips. Between measurements, the flocs were maintained in suspension with gentle magnetic stirring.

The maximum age of the preparations after a constant pH had been reached was 11 hr. These short times were designed to prevent extensive oxolation of the precipitated hydroxide and the formation of dissolved polynuclear hydroxo complexes by leaching.

For the determination of the ZPC by electrophoresis, aluminum nitrate nonahydrate was recrystallized twice from water. Aluminum hydroxide was precipitated by dropwise addition of ammonia to a stirred 0.01 M solution of aluminum nitrate heated to 80–90°. After cooling, it was washed repeatedly by centrifugation and further purified by electrodialysis. The aluminum hydroxide dispersions were diluted with equal volumes of sodium nitrate solutions containing various amounts of sodium hydroxide or nitric acid. Carbon dioxide was excluded by means of a nitrogen blanket. The ionic strength of the diluted dispersions was maintained constant at 0.010 M. Nitrate ions had been found to be indifferent counterions for ferric and aluminum oxides (2).

The dispersions were stirred gently for 48 hr prior to electrophoresis to permit the leaching of any formed hydroxo complexes and their adsorption on the hydroxide particles. Aging for an additional 5 days did not produce significantly different mobility values for the two dispersions tested. The maximum time elapsed between precipitation and electrophoresis was 2 weeks. Such short aging periods at room temperature did not produce significant crystallization of aluminum hydroxide (9).

Electrophoretic mobilities were measured with the commercial microelectrophoresis apparatus described previously (10), using the glass cell with a molybdenum cylinder as the anode and a platinum–iridium strip as the cathode. The temperature of the dispersions during the measurements varied from 22 to 25°, a variation unlikely to produce measurable changes in the electrophoretic mobility (11). The pH of the dispersions was measured before and after electrophoresis. The differences were 0.2 pH unit or less, except for two electrophoresis runs that were excluded from Fig. 1.

RESULTS

The observed pH_{SP} values of aluminum hydroxide fell in the 5.95–6.25 range with a mean of 6.10, in agreement with the majority of values reported in Ref. 7. This result corresponds to a pK_{SP} range of 32.7–31.5 and a mean of 32.08. Each point in Fig. 1 represents the average of eight electrophoresis measurements. Negative mobility values indicate that the particles are negatively charged and migrate to the anode. Interpolation of the plot of Fig. 1 to zero mobility places the ZPC of aluminum hydroxide at 8.52. The preferred value is 8.5 ± 0.2.

The new value for the solubility product of aluminum hydroxide, other values from Ref. 7, and ZPC values from Ref. 1 are listed in Table I, where pK_{SP} represents the logarithm of the reciprocal of the solubility product. For the equilibrium:

$$M(OH)_z(s) \rightleftharpoons M^{z+} + zOH^-$$

Scheme I
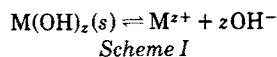
the following equation is readily derived for 24–25°, at which temperature the product of the concentrations of hydrogen and hydroxide ions of water

Table I—ZPC, Solubility Product, and Derived pH Value for Sparingly Soluble Metal Hydroxides

Cation	ZPC	pK_{SP}[a]	pH_{SP}[b]
Zirconium	6.7	50.8	3.96
Cerium(IV)	6.75	50.6	4.00
Chromium(III)	7.0	30.2	6.57
Mercury(II)	7.3	25.5	5.60
Iron(III)	8.6	37.5	4.75
Tin(II)	8.7	25.8	5.50
Yttrium	9.0	22.9	8.40
Aluminum	9.1 (8.5)	32.1	6.10
Zinc	9.3	16.4	8.63
Copper(II)	9.4	19.5	7.60
Beryllium	10.2	21.3	7.00
Lanthanum	10.4	19.8	9.17
Lead(II)	10.5	15.1	9.07
Cadmium	10.5	13.8	9.50
Nickel(II)	11.1	15.2	9.03
Cobalt(II)	11.4	14.8	9.17
Iron(II)	12.0	14.4	9.30
Magnesium	12.0	10.8	10.50
Manganese(II)	12.4	12.8	9.83

[a] The negative logarithm of the solubility product. [b] Defined by Eq. 1.

is equal to 1.00×10^{-14}:

$$pH_{SP} = 14.00 + \frac{\log z - pK_{SP}}{z + 1} \qquad \text{(Eq. 1)}$$

Regression analysis of the data in Table I produced the following two correlations. The nonlinear relationship between the ZPC and pK_{SP} can be represented by the equation:

$$ZPC = 15.41 - 0.355pK_{SP} + 0.00371pK_{SP}^2 \qquad \text{(Eq. 2)}$$

The values of F, of the coefficient of multiple correlation, and of the standard error of the estimate were 29.42, 0.917, and 0.869, respectively. The inclusion of a cubic term in Eq. 2 improved the precision only marginally.

The linear relationship between the ZPC and pH_{SP} is shown in Fig. 2 and can be represented by the equation:

$$ZPC = 3.82 + 0.764pH_{SP} \qquad \text{(Eq. 3)}$$

The values of F and of the correlation coefficient are 56.6 and 0.877, respectively. When the experimental difficulties in determining the ZPC and the lack of agreement among reported ZPC values for a single compound are considered, the scatter of data points about Eqs. 2 and 3 is not too serious.

The redetermined ZPC value of aluminum hydroxide, 8.5, is identical with the value of 8.48 calculated by Eq. 3. It is somewhat lower than the value of 9.1 given in Ref. 1 and higher than the value of 7.85 calculated by Eq. 2. The ZPC values for nickel and cobalt hydroxides were recently
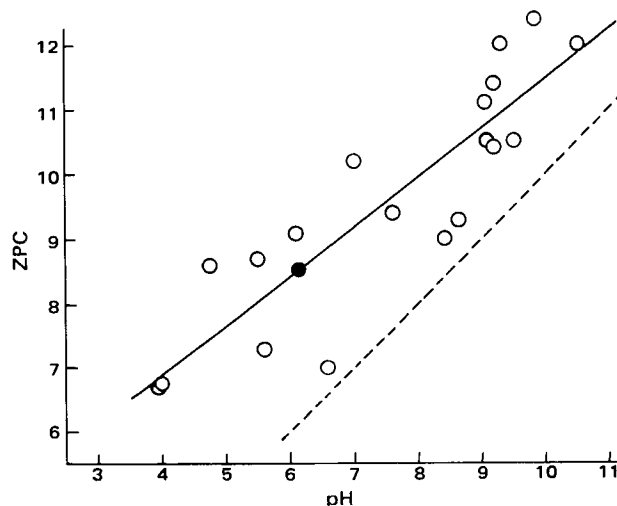

Figure 2—*The ZPC–pH_{SP} relation for slightly soluble hydroxides. The solid line represents the linear regression (Eq. 3); the broken line has a 45° or unit slope. The solid circle refers to the ZPC and pH_{SP} values of aluminum hydroxide determined in the present work.*

redetermined on thoroughly analyzed samples (11). The value found for nickel hydroxide, 11.1 ± 0.1, is identical with the value of Ref. 1 and close to the values of 10.88 and 10.72 calculated by Eqs. 2 and 3, respectively. Likewise, the ZPC value determined for cobaltous hydroxide, 11.5 ± 0.1, is nearly identical with the 11.4 value of Ref. 1 and in reasonable agreement with the values calculated by Eqs. 2 and 3, 10.97 and 10.83, respectively.

It is, therefore, possible to estimate the ZPC of an inorganic hydroxide from its solubility product or, more specifically, from the pK_{SP} or pH_{SP} value by means of Eq. 2 or 3, respectively.

DISCUSSION

The cations listed in Table I were arranged in order of increasing ZPC values which, according to Eq. 3, also corresponds to increasing pH_{SP} values. The ZPC and pH_{SP} values of the hydroxides generally increase as the valence of the cations decreases. The two tetravalent cations are at the top of the table, having the lowest ZPC and pH_{SP} values. All but two of the eight lowest ZPC values belong to tetravalent or trivalent cations, and 10 of the 11 highest ZPC values belong to divalent cations.

The ZPC of the hydroxide is always higher than its pH_{SP}. This result is shown in Fig. 2 by the fact that the straight line based on experimental data lies above the 45° or unit-slope line representing ZPC = pH_{SP}. For aluminum hydroxide, as an example, the ZPC value of 8.5 or 9.1 is 2.4 or 3.0 pH units higher than the pH_{SP} value of 6.1. At pH 6.1, the surface layer contains less hydroxide and more aluminum than the stoichiometric 3:1 ratio, while the solution contains these two ions in the exact 3:1 ratio.

There are two equivalent explanations to account for the difference between the ZPC and pH_{SP} or for the difference in the composition of the surface layer and the bulk of a hydroxide particle. Again, aluminum hydroxide is used for illustration. According to the first viewpoint, the trivalent aluminum ion is held more strongly in the aluminum hydroxide lattice than the monovalent hydroxide ion because of its higher valence. Hence, when the concentration of the two ions in solution is in the ratio of 1:3 (which occurs at pH_{SP} = 6.1), the negative hydroxide ions escape more readily from the surface layer, conferring a positive charge to the particle (12).

From an alternative viewpoint (13), a suspension of aluminum hydroxide contains the following potential-determining ions in solution: hydrated aluminum, possibly a polynuclear hydroxo complex of higher positive charge (e.g., 4+), and hydroxide ions. At pH 6.1, the former two are more extensively adsorbed from solution onto an aluminum hydroxide particle than the latter, based on the number of equivalents, because of their higher charge. The greater adsorption of cationic equivalents confers a positive charge to the particle. There is a continuous dynamic adsorption–desorption equilibrium between ions in solution and ions in the surface and the Stern layer of the hydroxide particles. According to both explanations, their higher charge is responsible for the greater retention or adsorption of the cations by the surface of the hydroxide particles when compared to the hydroxide anion, based on the number of equivalents.

As more hydroxide ions are added to the solution, the concentration of dissolved aluminum ions diminishes correspondingly to maintain the solubility product constant, and the adsorption of these two ions onto the particle surface approaches the stoichiometric 3:1 ratio. When the concentration of hydroxide ions is increased from pOH = 14.0 − 6.1 = 7.9 to pOH = 14.0 − 8.5 = 5.5, equivalent amounts of hydroxide and aluminum ions are adsorbed, rendering the particle surface neutral and reducing the charge of the particle to zero. At still higher hydroxide-ion concentrations, the particle becomes negatively charged because an excess of hydroxide ions chemisorbed in the surface layer produces aluminate ions in that layer, with a 4:1 ratio of hydroxide to aluminum ions (3).

Comparison of the slopes of the least-squares line of Fig. 2 represented by Eq. 3 and of the 45° line by means of the t test (14, 15) revealed that the value of the former, namely, 0.764, differs significantly from 1.000 despite the scatter of the experimental points. Since their two intercepts are also significantly different, the two straight lines are not parallel but will converge at a very high value of pH_{SP}.

In view of the variability of the ZPC values for different batches of a single hydroxide, the following two observations are presented to document the usefulness of knowing the ζ-potential of the pure hydroxide as a function of pH and its ZPC. In manufacturing hydroxide suspensions, it is important to achieve uniformity and to minimize batch-to-batch variations in the sedimentation volume, the viscosity, the tendency to cake, and, hence, in the surface charge density or ζ-potential at the pH of the suspension and in the ZPC.

It is known from practical experience (16) that the pH values for various batches of a given hydroxide differ little or not at all from the pH_{SP} of the pure hydroxide. The ζ-potentials of these batches at the pH_{SP}, on the other hand, often differ significantly from the ζ-potential of the pure hydroxide because of frequent deviations in their ZPC values from the value of the pure hydroxide by as much as 1 pH unit or more. Greater deviations in ζ-potential at the suspension pH and in ZPC from the corresponding values of the pure hydroxide frequently cause increased batch-to-batch variability in suspension properties and commensurately larger drifts of these properties with time.

Furthermore, the sign and magnitude of the deviation of the ZPC value of a batch from that of the pure hydroxide (or the sign and magnitude of the difference between their ζ-potentials at pH_{SP}) often indicate the cause of such a deviation. For instance, the large variation among the ZPC values reported for aluminum hydroxide (1) is probably due to its tendency to form soluble complexes of high positive valence (4, 17) which are leached from the precipitate and subsequently adsorbed on its surface.

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