Effect of Adsorbed Carbonate on Surface Charge Characteristics and Physical Properties of Aluminum Hydroxide Gel
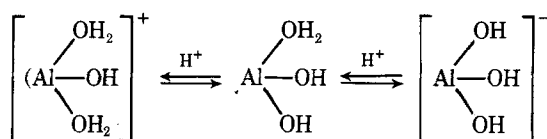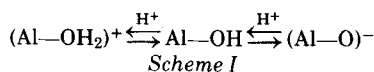
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Abstract ◻ A titration procedure was used to determine the zero point of charge of a number of chloride-containing aluminum hydroxide gels and aluminum hydroxycarbonate gels. The surface charge characteristics of aluminum hydroxide gel were determined by both hydroxyls and the surface density of specifically adsorbed carbonate anion. The wide range of zero point of charge values reported for aluminum hydroxide is thought to be due to the presence of specifically adsorbed anions such as carbonate. The effect of ionic strength on the pH of aluminum hydroxide gel is important during washing since the ease of electrolyte removal is related to surface charge. Viscosity and sedimentation characteristics are related to the relationship between the zero point of charge and bulk pH. Maximum viscosity was observed when the bulk pH was adjusted to the zero point of charge.

Keyphrases ◻ Aluminum hydroxide gel—effect of adsorbed carbonate on surface charge and physical characteristics ◻ Carbonate, adsorbed—effect on surface charge and physical characteristics of aluminum hydroxide gel ◻ Physicochemistry—effect of adsorbed carbonate on surface charge and physical characteristics of aluminum hydroxide gel

Aluminum hydroxide gels exhibit a surface charge whose sign and magnitude depend on bulk pH, specific ion adsorption, and ionic strength. When no specific adsorption of ions other than protons or hydroxyls occurs, as with chloride- or nitrate-containing aluminum hydroxide gels (1), surface charge arises by the mechanism (2) shown in Schemes I and II (which are equivalent). For clarity, only the bonds associated with the charged site are shown, even though aluminum is in sixfold coordination in each structure.

$$(Al\!-\!OH_2)^+ \underset{}{\overset{H^+}{\rightleftharpoons}} Al\!-\!OH \underset{}{\overset{H^+}{\rightleftharpoons}} (Al\!-\!O)^-$$

Scheme I

$$\left[\begin{matrix} & OH_2 \\ (Al\!-\!OH) \\ & OH_2 \end{matrix} \right]^+ \overset{H^+}{\rightleftharpoons} \begin{matrix} & OH_2 \\ Al\!-\!OH \\ & OH \end{matrix} \overset{H^+}{\rightleftharpoons} \left[\begin{matrix} & OH \\ Al\!-\!OH \\ & OH \end{matrix} \right]^-$$

Scheme II

When carbonate or any other specifically adsorbed anion (1) is present as in aluminum hydroxycarbonate gel, a second mechanism (Scheme III) contributes to the surface charge. Thus, the observed surface charge of aluminum hydroxycarbonate gel depends on the surface density of each type of site.

$$Al\!-\!OH + CO_3^{2-} \rightleftharpoons Al\!-\!OCO_2^- + OH^-$$

Scheme III
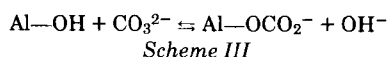
An important property of colloidal systems that possess a pH-dependent surface charge is the zero point of charge, which is the pH at which the net surface charge is zero. At this pH, the densities of the positive and negative charges arising from Schemes I–III are equal (3).

A number of anions other than carbonate affect the zero point of charge of metal oxides through specific adsorption to metal oxide surfaces. These anions include orthophosphate, pyrophosphate, tripolyphosphate, silicate, selenite, and fluoride anions (4). In each case, the specifically adsorbed anion contributes additional negative charge to the surface, thereby displacing the zero point of charge to lower pH values. The major objective of this study was to determine the effect of specifically adsorbed carbonate on the zero point of charge. Another objective was to illustrate the effect of surface charge on important physical properties such as apparent viscosity and electrolyte removal by washing.

EXPERIMENTAL

Materials—Two chloride-containing aluminum hydroxide gels were prepared in an identical manner, with precautions taken to minimize the specific adsorption of carbonate. A closed, baffled reaction vessel was used as well as freshly distilled water stored in a closed container. Potassium hydroxide (1 M) was added with continuous stirring to 0.5 M AlCl₃ at 1 ml/min through a submerged delivery tube having a pinhole-size orifice until pH 9.5 was reached. The resulting chloride-containing aluminum hydroxide gel was allowed to stand for 24 hr and was washed with five volumes of freshly distilled water using centrifugation.

An aluminum hydroxycarbonate gel was prepared by the addition of 0.5 M AlCl₃ to a solution of 0.5 M NaHCO₃ and 0.23 M Na₂CO₃ with agitation until pH 6.6 was reached (5). The aluminum hydroxycarbonate gel was allowed to stand for 24 hr and was washed with five volumes of water using centrifugation.

Nine aluminum hydroxycarbonate gels were obtained commercially.

Analytical Procedures—The titration technique (6) used to measure the zero point of charge was based on the principle that changes in the ionic strength produced by the addition of an indifferent electrolyte, such as potassium chloride, will have no effect on proton adsorption or release by the gel when the gel surface charge is zero. Thus, titration curves (moles of bound or released protons *versus* pH) obtained at several ionic strengths intersect at a common point, the zero point of charge.

The zero point of charge of the laboratory chloride-containing aluminum hydroxide gels and the laboratory aluminum hydroxycarbonate gel was determined by the following procedure. Aliquots of the gel containing ~1% equivalent aluminum oxide were prepared containing the appropriate quantities of potassium chloride and hydrochloric acid or potassium hydroxide, depending on the ionic strength and pH desired. The amount of hydrochloric acid or potassium hydroxide added and the resulting pH were recorded. A blank, i.e., no gel present, also was treated similarly to correct for any acid or base that did not result in the adsorption or release of protons from the surface. Curves obtained at different ionic strengths intersect at the zero point of charge. A correction was rarely needed, and a more rapid and convenient continuous titration procedure was developed for routine use.

The zero point of charge of the commercial aluminum hydroxycarbonate gels were determined by a continuous titration procedure. An aluminum hydroxycarbonate gel sample, adjusted to the desired ionic strength with potassium chloride, was titrated with either acid or base, depending on the desired direction of pH change. A blank titration was not run since experience showed that no significant correction was needed. The recorded pH values and the corresponding quantity of acid

Table I—Zero Point of Charge (ZPC) of Laboratory and Commercial Aluminum Hydroxide Gels

Sample	ZPC	Bulk pH	Apparent Surface Charge
Laboratory chloride-containing aluminum hydroxide gel 1	9.65	8.00	+
	9.65	8.00	+
	9.65	8.00	+
Laboratory chloride-containing aluminum hydroxide gel 2	9.68	8.00	+
Laboratory aluminum hydroxycarbonate gel	6.65	7.05	−
	6.67	7.05	−
	6.66	7.05	−
Commercial aluminum hydroxycarbonate gel 1	6.95	6.34	+
	6.95	6.34	+
	6.95	6.34	+
Commercial aluminum hydroxycarbonate gel 2	6.64	6.38	+
Commercial aluminum hydroxycarbonate gel 3	7.32	5.80	+
Commercial aluminum hydroxycarbonate gel 4	6.30	6.25	+
Commercial aluminum hydroxycarbonate gel 5	6.53	6.51	~0
Commercial aluminum hydroxycarbonate gel 6	6.54	6.60	−
Commercial aluminum hydroxycarbonate gel 7	6.68	6.56	+
Commercial aluminum hydroxycarbonate gel 8	6.90	6.17	+
Commercial aluminum hydroxycarbonate gel 9	6.94	5.63	+

or base added were plotted, and the intersection point of the different ionic strength curves was the zero point of charge, i.e., the pH at which ionic strength has no effect.

The specific procedure was as follows:

1. A 100-ml aliquot containing ~1% equivalent aluminum oxide was transferred to a 250-ml beaker.

2. The initial pH was recorded with stirring after a stable value was achieved.

3. Sufficient 0.1 N KOH was added from a 10-ml buret to cause a pH change of 0.05–0.10 unit. Usually, increments of titrant ranging from 0.2 to 1.0 ml were required. When the pH was stable, the volume of titrant added and the pH were recorded.

4. Steps 1–3 were repeated but titration was performed with 0.1 N HCl.

5. A plot was constructed with micromoles of acid or base added on the ordinate and the resultant pH on the abscissa.

6. Steps 1–5 were repeated except that, in Step 1, 2 ml of 4 M KCl was added to the 100-ml volumetric flask before making the final dilution of the ~1% equivalent aluminum oxide aliquot. The data were plotted on the same graph.

7. Steps 1–5 were repeated except that, in Step 1, 10 ml of 4 M KCl was added to the 100-ml volumetric flask before making the final dilution of the ~1% equivalent aluminum oxide aliquot. The data were plotted on the same graph. The pH where the three curves intersected was the zero point of charge.

The equivalent aluminum oxide content was determined by the ethylenediaminetetraacetic acid titration (7).

Viscosity measurements were made on two of the commercial aluminum hydroxycarbonate gels after the gel pH was adjusted to selected values above and below the zero point of charge. The pH range of 5–9.5 was selected to avoid substantial solubilization of the aluminum hydroxycarbonate gel (8). Two hundred milliliters of a gel containing 9% equivalent aluminum oxide was adjusted to the desired pH by the addition of either 1 N HCl or KOH. The ionic strength of all samples was adjusted to 0.03 by adding 1 M KCl. The final volume of all samples was adjusted to 230 ml with distilled water. Each sample was vigorously stirred and transferred into the measuring vessel of the rotational viscometer[1] with the appropriate spindle in place. Each sample was allowed to set for 5 min before the viscosity was measured at 100 rpm.

RESULTS AND DISCUSSION

Figure 1 illustrates the zero point of charge determination of the laboratory chloride-containing aluminum hydroxide gel 1. The value is concluded to be 9.65 because ionic strength did not affect the gel at pH 9.65. Triplicate determinations resulted in identical results (Table I), indicating the excellent precision of the individual sample adjustment method for determining the zero point of charge. The precipitation method also was very reproducible since the zero point of charge of lab-
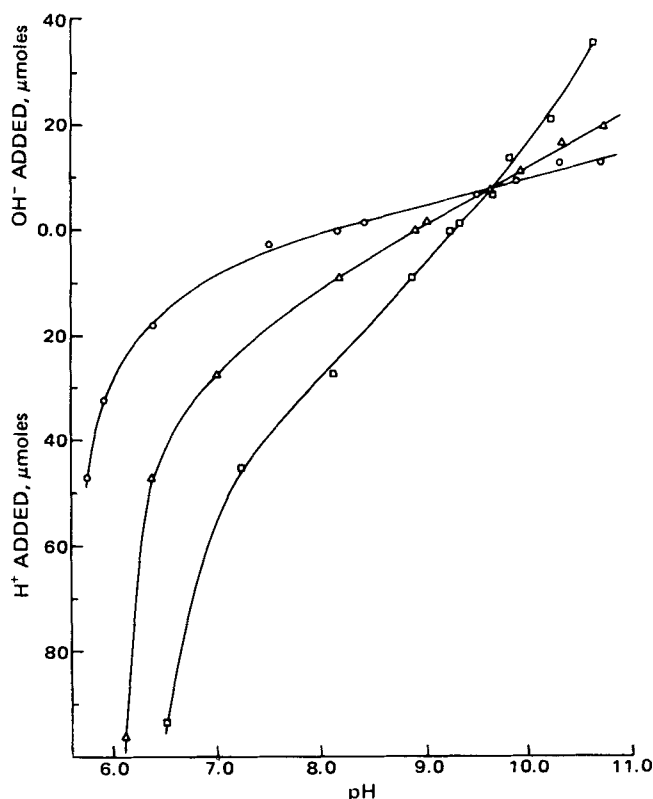
[1] Model RVT, Brookfield Engineering Laboratories, Stoughton, Mass.

Figure 1—*Determination of the zero point of charge of laboratory chloride-containing aluminum hydroxide gel 1. Key: O, μ = 0.0005; Δ, μ = 0.01; and $\Box$, μ = 0.6.*

oratory chloride-containing aluminum hydroxide gel 2 was 9.68 (Table I). The surface charge of both gels was positive since the bulk pH was below the zero point of charge.

Specifically adsorbed carbonate had a substantial effect on the zero point of charge. The value of the laboratory aluminum hydroxycarbonate gel was 6.66 ± 0.01 based on triplicate determinations (Table I). The surface charge of this gel was negative since the bulk pH was above the zero point of charge.

The continuous titration method also measured precisely the zero point of charge; triplicate determinations on commercial aluminum hydroxycarbonate gel 1 gave identical results of 6.95 (Table I). The zero point of charge of the nine commercial aluminum hydroxycarbonate gels ranged from 6.3 to 7.3. These gels exhibited positive, neutral, and negative surface charges. The lower and more variable values obtained for the aluminum hydroxycarbonate gels in comparison to the chloride-containing aluminum hydroxide gels indicate that specifically adsorbed carbonate contributes to the surface charge characteristics as hypothesized in Scheme III.

The zero point of charge of the chloride-containing aluminum hydroxide gel was similar to values reported for highly crystalline forms of aluminum hydroxide (9), which would be expected to be largely free of specifically adsorbed carbonate. This finding suggests that chloride, like nitrate, is outside the coordination sphere of the aluminum cation and interacts by electrostatic forces (1). This observation agrees with an earlier observation that a chloride impurity in hydrous aluminum oxide does not affect the zero point of charge (9).

Thus, it appears that the wide range of zero point of charge values, i.e., 3.8–10.0 (9, 10), reported for aluminum hydroxide is due to the presence of a specifically adsorbed anion such as carbonate that contributes to the surface charge characteristics (Scheme III) in addition to the contribution of surface hydroxyls (Schemes I and II). Direct adsorption of carbon dioxide from the atmosphere by aluminum hydroxide is likely to occur since carbon dioxide is known to be strongly adsorbed onto moist goethite surfaces as carbonate (11).

The effect of ionic strength on the pH of aluminum hydroxide is seen in Fig. 1. As the ionic strength increased, the pH of the aluminum hydroxide gel tended toward the zero point of charge. Conversely, lowering the ionic strength caused the pH to move away from the zero point of charge. This behavior must be considered during the washing of aluminum hydroxide gel or the final pH of the gel after washing will be un-
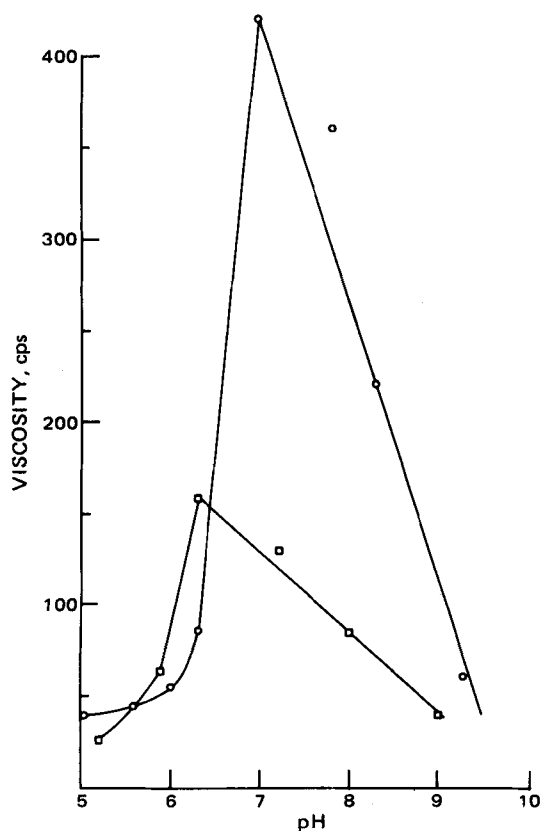
Figure 2—*Effect of bulk pH on apparent viscosity of commercial aluminum hydroxycarbonate gels 1 (O) and 4 (□). The zero point of charge of commercial aluminum hydroxycarbonate gels 1 and 4 are 6.95 and 6.30, respectively.*

predictable. Table I indicates that the bulk pH ranged from 5.63 to 6.60 and was as random as the zero point of charge. Figure 1 indicates that washing a gel whose pH was at the zero point of charge did not produce a pH change even though the ionic strength was reduced. Furthermore, because the gel surface is neutral when the pH is at the zero point of charge, electrolyte removal should be accomplished most readily when washing is performed under these conditions. Cations will be retained if washing occurs at pH conditions above the zero point of charge, and anions will be retained if the pH during washing is below the zero point of charge.

Physical properties of aluminum hydroxide gel such as viscosity and sedimentation characteristics are controlled largely by a sensitive interplay between the attractive and repulsive forces operating between the particles and aggregates. The coulombic repulsive force and the van der Waals attractive force are of prime importance. For molecules, van der Waals forces are weak and very short ranged, with the force being inversely proportional to the seventh power of the distance separating the molecules (12). Only in the absence of other forces and at sufficiently low temperatures do these forces manifest themselves between molecules. For particles, the situation is different. To find the magnitude of the force and the dependence on the separating distance, the assumption is often made that the individual forces operating between molecules may be summed pairwise to obtain the net force between macroscopic bodies (12). In the case of two flat slabs, where the separation distance is small compared to the thickness of either slab, the force varies inversely with the third power of the separating distance. The van der Waals force summed in this way has sufficient magnitude to be of relevance in colloidal systems. In fact, when the charge on the particle surfaces is sufficiently reduced (by adjustment of pH or ionic strength), the van der Waals forces are responsible for aggregation and associated phenomena (13). A result similar to that obtained for flat slabs also occurs for macroscopic spheres.

Another important result related to van der Waals forces is that the force between anisometric particles is a function of the relative orientations of the bodies (considering all orientations having the same center of mass separation). In particular, lath-shaped particles and needles interact most strongly when positioned end-to-end. Plates interact most strongly in an edge-to-edge orientation. For isometric particles, the same considerations apply since joining two isometric particles necessarily forms an anisometric aggregate which tends to orient itself end-on with a third particle (12).

The apparent viscosity of aluminum hydroxide gel is sensitive to the bulk pH because of particle interactions. When coulombic repulsion is sufficiently reduced by adjusting the bulk pH close to the zero point of charge or by increasing the ionic strength, the van der Waals forces cause the particles to agglomerate. Consequently, the apparent viscosity increases. The magnitude of the viscosity change depends on the aggregate structures. Figure 2 illustrates the effect of bulk pH on the apparent viscosity of commercial aluminum hydroxycarbonate gels 1 and 4. The viscosity of both aluminum hydroxycarbonate gels was at a maximum when the bulk pH was at the zero point of charge, i.e., pH 6.95 and 6.30, respectively. The fact that a different maximum viscosity occurred for each aluminum hydroxycarbonate gel suggests that aluminum hydroxycarbonate gel 1 formed a more highly extended and cross-linked network of particles in comparison to aluminum hydroxycarbonate gel 4.

The apparent viscosity of aluminum hydroxycarbonate gel 1 increased eightfold as the pH increased from 5.95 to 6.95, and aluminum hydroxycarbonate gel 4 showed a sixfold increase in apparent viscosity between pH 5.30 and 6.30. A small pH change in the region of the zero point of charge produces large changes in apparent viscosity.

It is apparent from Fig. 2 that investigations of the factors affecting aggregate type will prove valuable because aluminum hydroxide gels whose apparent viscosity is not sensitive to small variations in bulk pH are more generally desirable. In addition, the pH changes that may occur when aluminum hydroxide gel is washed also may lead to changes in viscosity. Finally, the results suggest that the viscosity of aluminum hydroxide gels can be controlled by adjusting the relationship between the zero point of charge and the bulk pH to produce the desired degree of aggregation.

REFERENCES

(1) C. J. Serna, J. L. White, and S. L. Hem, Soil Sci. Soc. Am. J., 41, 1009 (1977).

(2) T. W. Healy and L. R. White, Adv. Colloid Interface Sci., 9, 303 (1978).

(3) R. G. Gast, in "Minerals in Soil Environments," J. B. Dixon and S. B. Weed, Eds., Soil Science Society of America, Madison, Wis., 1977, pp. 27–73.

(4) F. J. Hingston, R. J. Atkinson, and J. P. Quirk, Nature, 215, 1459 (1967).

(5) S. L. Hem, E. J. Russo, S. M. Bahal, and R. S. Levi, J. Pharm. Sci., 59, 317 (1970).

(6) T. F. Tadros and J. Lyklema, J. Electroanal. Chem., 17, 267 (1968).

(7) "The United States Pharmacopeia," 20th rev., United States Pharmacopeial Convention, Rockville, Md., 1980, p. 25.

(8) J. D. Hem and C. E. Robertson, Geological Survey Water-Supply Paper 1827-A, U.S. Government Printing Office, Washington, D.C., 1967, p. 147.

(9) G. A. Parks, Chem. Rev., 65, 177 (1965).

(10) H. Schott, J. Pharm. Sci., 66, 1548 (1977).

(11) J. D. Russell, E. Patterson, A. R. Fraser, and V. C. Farmer, J. Chem. Soc., Faraday Trans., 71, 1623 (1975).

(12) J. Mahanty and B. W. Ninham, "Dispersion Forces," Academic, London, England, 1976, pp. 11, 16, 21, 22.

(13) H. Van Olphen, "An Introduction to Clay Colloid Chemistry," Wiley–Interscience, New York, N.Y., 1977, p. 36.