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SURFACE CHARGE CHARACTERISTICS OF ALUMINUM HYDROXYCARBONATE AS INFLUENCED BY CARBONATE EQUILIBRIUM

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ABSTRACT

The isoelectric point of aluminum hydroxycarbonate suspension increases upon dilution with deionized water. The increase in the isoelectric point is directly related to the degree of dilution. Dilution with bicarbonate ion-containing solutions reduced the change in isoelectric point in comparison to dilution with deionized water. The change in isoelectric point was inversely related to the concentration of bicarbonate ion in the diluting solution. The increase in isoelectric point observed following dilution with deionized water was reversed by the addition of bicarbonate ion. The observations suggest that carbonate ions occupying potential

determining sites in the primary particles are in equilibrium with carbonate/bicarbonate ions in solution. Formulation or processing factors which affect the equilibrium will affect the isoelectric point of aluminum hydroxycarbonate suspensions and will influence their physical properties.

INTRODUCTION

Aluminum hydroxycarbonate suspensions exhibit surface charge characteristics arising from two separate mechanisms: ionization of surface hydroxyls and specific adsorption of carbonate anion (1). Hydroxyls at the surface of aluminum hydroxycarbonate particles undergo protonation/deprotonation reactions in response to the pH with an equivalence point of approximately 9.6 (1). Below this pH value the majority of the hydroxyl groups are protonated and exhibit a positive charge, while at pH's above 9.6, the deprotonation reaction dominates and most of the surface hydroxyls bear a negative charge. Specific adsorption of carbonate anion contributes additional negative charge to the surface and lowers the equivalence point.

The surface electrochemical behavior of an aluminum hydroxycarbonate suspension is a result of contributions by the previously mentioned two mechanisms. Previous studies (2-4) have suggested that specifically adsorbed carbonate anions in aluminum hydroxycarbonate suspensions are in equilibrium with carbonate anions in solution. These ions are then in equilibrium with carbon dioxide in the air. Because many physical properties of aluminum hydroxycarbonate suspensions are affected by the surface charge characteristics (5-7), a study was undertaken to further investigate the hypothesis that specifically adsorbed carbonate anion is in equilibrium with carbonate ion in solution.

MATERIALS AND METHODS

A commercial aluminum hydroxycarbonate suspension containing 17.2% w/w equivalent Al_2O_3 (Barcroft) was studied. The equivalent aluminum oxide content was determined by chelatomeric titration (8) and was expressed as aluminum concentration, e.g., 17.2% w/w equivalent Al_2O_3 is equal to 3.37 mmol Al/g. The carbonate content was determined by gasometric displacement (9) using the Chittick apparatus (Sargent-Welch) and expressed as the carbonate to aluminum molar ratio. The modification proposed by Scholtz et al. (3) to ensure temperature control was employed.

Samples were prepared by weighing the appropriate amount of aluminum hydroxycarbonate suspension into a polyethylene bottle and then adding sufficient diluting media (deionized water or potassium bicarbonate solution) to make 400 g. The suspension was then stirred for 15 min. to ensure uniformity. Aliquots of 20 g were removed and the pH adjusted by the dropwise addition of 0.1 N KOH or 0.1 N HCl using a calibrated pipette with constant stirring over a 5 min. time period. The total number of drops added was brought to 100 with 0.1 M KCl. In this manner, samples were prepared at the desired pH, but the solids content and ionic strength were constant for each set of samples. The ionic strength that would result from the addition of 100 drops of any of the above solutions to 20 g of deionized water was 15.6 mM.

Zeta potential measurements of the samples were made by Doppler electrophoretic light scattering (DELSA 440, Coulter). As the measurement requires the passage of laser light through the sample, samples were centrifuged (GLC-1, Sorvall) at 3000 rpm for 2 min. prior to analysis. Some of the particles from the resulting porous plug were redispersed into the clear supernatant. The supernatant was then decanted and used for determination of the zeta potential. The pH at which the zeta potential is equal to zero was taken as the isoelectric point. This parameter is similar to the point of zero charge which has also been used to characterize the surface charge of aluminum hydroxycarbonate suspensions (2).

RESULTS

The effect of pH on the zeta potential of the aluminum hydroxycarbonate suspension at 4 degrees of dilution is shown in Figure 1. The isoelectric point increased from 7.0 to 8.2 as the suspension was diluted with deionized water from 1.0 mmol Al/g to 0.016 mmol Al/g.

Since the carbonate to aluminum molar ratio has been shown to be inversely related to the point of zero charge of a series of aluminum hydroxycarbonate suspensions measured at the same solids content (4), this parameter was determined for each of the dilutions presented in Figure 1. The carbonate to aluminum ratios for all 4 dilutions as well as the undiluted suspension was 0.39. Thus, the total carbonate content of the system was unaffected by dilution with deionized water.

It has been shown that it is the specifically adsorbed carbonate anion at the particle surface which causes the point of zero charge of aluminum hydroxycarbonate to be lowered with respect to aluminum hydroxide (1, 10). In addition, the

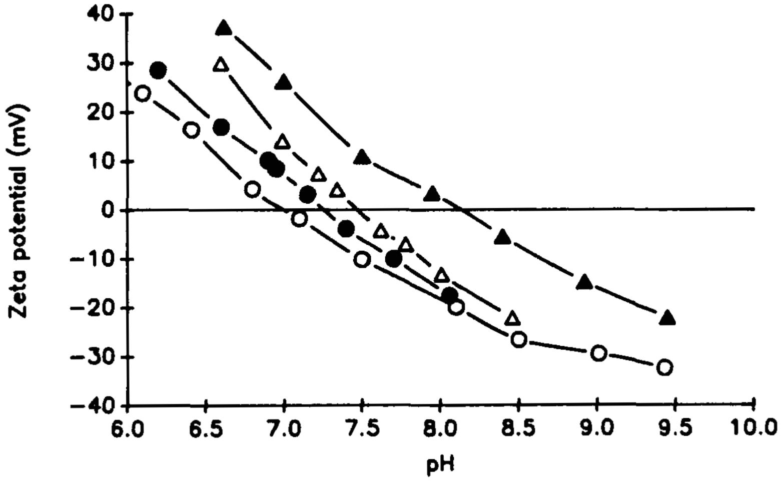

Figure 1 - Effect of pH on the zeta potential of an aluminum hydroxycarbonate suspension at different degrees of dilution with deionized water. Key: ○, 1.0 mmol Al/g; ●, 0.74 mmol Al/g; △, 0.13 mmol Al/g; ▲, 0.016 mmol Al/g.

specifically adsorbed carbonate anion is believed to be in equilibrium with dissolved carbonate anion in the media surrounding the particles (4). Since the carbonate to aluminum molar ratio was found to be constant throughout the dilutions but the isoelectric points increased with increased water content, it was thought that carbonate ion was being desorbed from the surface of the particles and entering into solution. If this hypothesis is correct, the presence of carbonate ion in the diluting solution would be expected to reduce the desorption of specifically adsorbed carbonate ion, and hence, to reduce the change in isoelectric point.

The aluminum hydroxycarbonate suspension containing 3.37 mmol Al/g was diluted to 0.6 mmol Al/g using either deionized water or potassium bicarbonate solutions of various concentrations. Potassium bicarbonate was used to provide a soluble source of carbonate ions in order to prevent dissolution of aluminum hydroxycarbonate that may be caused by highly alkaline solutions of dibasic carbonate salts such as sodium carbonate or potassium carbonate. As seen in Figure 2, the isoelectric point of the sample diluted with water was the highest, 7.4. Dilution to the same solids content using various potassium bicarbonate solutions resulted in lower isoelectric points. The isoelectric points determined from Figure 2 are presented in Table I. The data in Table I show that the isoelectric point was inversely related to the concentration of potassium bicarbonate in the diluting solution supporting the hypothesis that specifically adsorbed carbonate anion is in equilibrium with carbonate ion in solution.

In order to further test the hypothesis, an additional sample was first exposed to deionized water

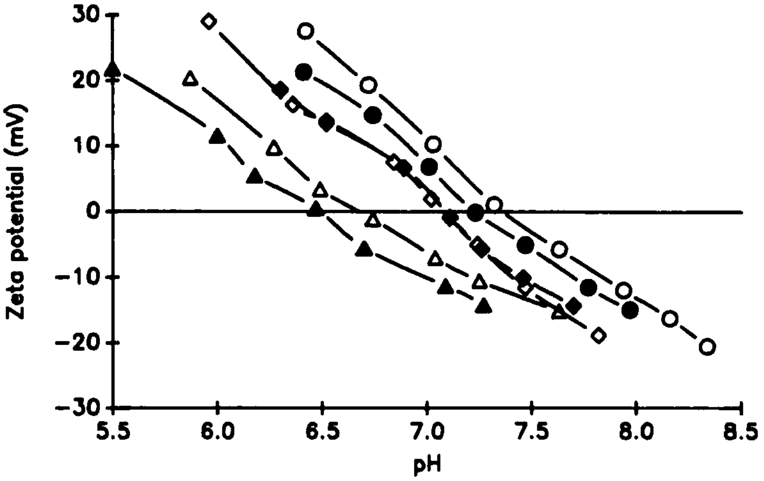

Figure 2 - Effect of pH on the zeta potential of an aluminum hydroxycarbonate suspension diluted to 0.6 mmol Al/g with various diluting solutions. Key: ○, deionized water; ●, 0.010 M $KHCO_3$; ◇ , 0.025 M $KHCO_3$; △ , 0.100 M $KHCO_3$; ▲ , 0.500 M $KHCO_3$; ⬤ , equilibrated in deionized water for 24 h then $KHCO_3$ added to produce 0.025 M $KHCO_3$.

to desorb carbonate anion and then to a potassium bicarbonate solution. Briefly, the sample was diluted to the desired aluminum content (0.6 mmol Al/g) with deionized water and made uniform by mixing. At this point the sample was identical to the sample diluted with deionized water in Figure 2 which demonstrated an isoelectric point of 7.4. After 24 hours of undisturbed aging at room temperature, a small portion

Table I - Effect of Carbonate Ion Concentration in the Diluting Solution on the Isoelectric Point of an Aluminum Hydroxycarbonate Suspension Containing 0.6 mmol Al/g.

Diluting Solution	Isoelectric Point
Deionized water	7.4
0.010 M $KHCO_3$	7.3
0.025 M $KHCO_3$	7.1
0.100 M $KHCO_3$	6.7
0.500 M $KHCO_3$	6.5

of the clear supernatant which was produced by centrifugation was removed and replaced with an equal volume of 1.0 M potassium bicarbonate such that the final composition was equivalent to the sample diluted with 0.025 M potassium bicarbonate in Fig. 2. The zeta potential vs pH curve after addition of the potassium bicarbonate was essentially identical to that of the sample originally diluted with 0.025 M potassium bicarbonate (Fig. 2). Thus, it is clear that specifically adsorbed carbonate anions that have been desorbed from the particle surface can be readsorbed in response to a change in the concentration of carbonate ion in solution. This behavior confirms that specifically adsorbed carbonate ions are in equilibrium with carbonate ions in solution in aluminum hydroxycarbonate suspensions.

DISCUSSION

The isoelectric point of an aluminum hydroxycarbonate suspension was found to increase upon dilution with deionized water due to desorption of carbonate anions from potential-determining sites on the particles. In the limit of infinite dilution, therefore, the isoelectric point would be expected to approach that of an aluminum hydroxide suspension as mass action would result in all of the carbonate ions being desorbed from the surfaces of the particles. The isoelectric points of the aluminum hydroxycarbonate suspension at the various degrees of dilution with deionized water as well as that for an aluminum hydroxide gel in the absence of carbonate, 9.6, (10) are plotted in Figure 3. A gradual but significant increase in isoelectric point is noted as the concentration decreases from 1.0 mmol Al/g to 0.13 mmol Al/g (i.e. up to approximately 25-fold dilution of the original suspension). In comparison, as the solids content approaches zero, (e.g. 0.016 mmol Al/g or 211-fold dilution) the isoelectric point more

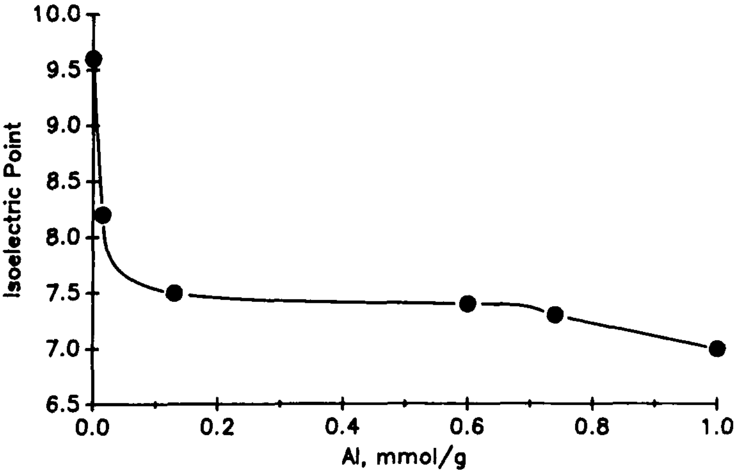

Figure 3 - Effect of dilution with deionized water on the isoelectric point of an aluminum hydroxycarbonate suspension. The suspension is expected to exhibit an isoelectric point corresponding to aluminum hydroxide, 9.6, at infinite dilution, i.e., Al concentration equals zero.

rapidly approaches that of aluminum hydroxide (plotted at 0.0 mmol Al/g). This behavior is consistent with equilibrium between specifically adsorbed carbonate anion and carbonate anion in solution and suggests that the magnitude of the effect of dilution depends on the concentration of the aluminum hydroxycarbonate suspension.

The distribution of carbonate anion in aluminum hydroxycarbonate suspensions has been previously described. Specifically adsorbed carbonate anion in unidentate coordination to aluminum is present at the surface of the primary particles (11). Carbonate anion is also present in the Stern and diffuse ionic layers surrounding the particles, but is easily exchanged or removed from these sites (10). Kerkhof (12) suggested that dilution with water is sufficient to alter the equilibrium between ions in the aluminum hydroxide structure and in solution, but did not address the identity or location of the ions. Later, Scholtz, et al., (3) demonstrated that even specifically adsorbed carbonate anion was in equilibrium with dissolved carbonate anion in aluminum hydroxycarbonate suspensions and demonstrated that removal of carbonate anion from solution favors desorption of the anion from the surface of the suspended particles.

Several reports have demonstrated the importance of carbonate anion in the aluminum hydroxycarbonate structure both in stabilizing against the development of order (2, 12) and imparting the favorable acid neutralization profiles (13, 14). The present study confirms the theory that dilution of an aluminum hydroxycarbonate suspension with deionized water leads to the movement of carbonate anion from potential-determining sites (i.e., in ligand coordination to the particle surface and in the Stern layer) into the aqueous media. Furthermore, this seems to be an equilibrium effect which is reversible suggesting that structural carbonate anion desorbed during the manufacture, packaging or transportation of aluminum hydroxycarbonate suspensions may be replaced, at least within the short time period following desorption when no significant aging has taken place.

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