

time, such as substantial desalting of the filtered effluent resulting from the polarization of the membranes and filters in the cell and density instability resulting from electrodecentration. The possibility of looser packing of the filter cake under the effect of the applied field, of surface conductance through the pores, and of the electroosmotic flow has also to be considered.

SUMMARY

Forced-flow electrophoresis has been applied to filtration of coarsely suspended particles using bentonite clay. If sufficient voltage is applied, constant filtration rates are obtainable without formation of filter cake. The inherent electroosmotic flow through the filter medium and filter cake has to be considered in the interpretation of data according to conventional filtration equations. Electrophoretic and electroosmotic effects are additive, giving increased rates of filtration, but a detailed theory cannot as yet be formulated.

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The Zero Point of Charge of Calcite

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The zero point of charge (ZPC) of calcite was investigated by measuring the streaming potential, solution equilibrium, and flotation response as a function of solution pH. The ZPC was shown to lie within the range of pH 8 to 9.5.

Thermodynamic calculation of the solution equilibrium suggests that the potential-determining ions are Ca^{++} , HCO_3^- , CO_3^{--} , H^+ , and OH^- .

Mechanisms of charge development at the calcite-water interface are discussed. The preferential hydrolysis of surface ions or the adsorption, at the interface, of the complexes formed in solution appears to play an important part in establishing the surface charge. Solutions with an initial pH near the isoelectric point showed a change in zeta potential and pH initially in one direction and later in the opposite direction, suggesting that a combination of fast and slow reactions is responsible for the charge development at the interface.

INTRODUCTION

Knowledge of the properties of the solid-liquid interface is necessary to understand interfacial phenomena such as flocculation, adsorption, and flotation. The interfacial properties of simple oxides and silicates in solution have been studied in detail, but little work has been done with salt-type minerals such as calcite to understand the mechanism of charge development at the interface. Although the solubility of calcite has been studied widely (1-5), few electrokinetic studies have been made to determine the zeta potential (6, 7), and one cannot obtain the zero point of charge from these electrokinetic studies, since the sign of the surface potential remains unchanged at all pH values that were studied.

It is the purpose of this study to determine the zero point of charge (ZPC), to identify the potential-determining ions, and to propose a mechanism for the creation of the surface charge on calcite.

It is well accepted that when a solid dissolves, both negative and positive species are present in solution and that there exists

a particular condition called the isoelectric point (IEP) (8) at which the two charges are equivalent electrically. A similar situation prevails at the solid-solution interface, particularly for oxides and silicates, for which H^+ and OH^- have been shown to be potential determining (9). At some particular solution pH the surface will be electrically neutral, and this pH will identify the zero point of charge. When the solution pH is more basic than the ZPC, negative ions and complexes will predominate at the interface and the surface will be negatively charged. Similarly, when the solution pH is more acidic than the ZPC, positive species will predominate and the surface will be positively charged. The close correspondence between the isoelectric point of the solution and the zero point of charge of the solid lead to the postulate (10) that they are governed by the same equilibrium which can be calculated from thermodynamic solubility data.

Calcite, when dissolved in water, will produce the following chemical species, H_2CO_3 , HCO_3^- , CO_3^{--} , Ca^{++} , CaHCO_3^+ ,

CaOH^+ , $\text{Ca}(\text{OH})_2(\text{aq})$, and $\text{CaCO}_3(\text{aq})$ by the following reactions: with other methods for determining the ZPC.

			Reference
[1] $\text{CaCO}_3(\text{s})$	$\rightleftharpoons \text{CaCO}_3(\text{aq})$	$K_1 = 10^{-5.00}$	"
[2] $\text{CaCO}_3(\text{aq})$	$\rightleftharpoons \text{Ca}^{++} + \text{CO}_3^{--}$	$K_2 = 10^{-3.25}$	"
[3] $\text{CO}_3^{--} + \text{H}_2\text{O}$	$\rightleftharpoons \text{HCO}_3^- + \text{OH}^-$	$K_3 = 10^{-3.47}$	(1, 11)
[4] $\text{HCO}_3^- + \text{H}_2\text{O}$	$\rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-$	$K_4 = 10^{-7.45}$	(1, 12)
[5] H_2CO_3	$\rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}$	$K_5 = 10^{1.47}$	(1, 13)
[6] $\text{Ca}^{++} + \text{HCO}_3^-$	$\rightleftharpoons \text{CaHCO}_3^+$	$K_6 = 10^{0.32}$	(14)
[7] CaHCO_3^+	$\rightleftharpoons \text{H}^+ + \text{CaCO}_3(\text{aq})$	$K_7 = 10^{-7.90}$	(14)
[8] $\text{Ca}^{++} + \text{OH}^-$	$\rightleftharpoons \text{CaOH}^+$	$K_8 = 10^{1.40}$	(15)
[9] $\text{CaOH}^+ + \text{OH}^-$	$\rightleftharpoons \text{Ca}(\text{OH})_2(\text{aq})$	$K_9 = 10^{1.47}$	"
[10] $\text{Ca}(\text{OH})_2(\text{aq})$	$\rightleftharpoons \text{Ca}(\text{OH})_2(\text{s})$	$K_{10} = 10^{2.45}$	"

* K_1 calculated from the equilibrium constant for the reactions [3], [6], [7] and [11] $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{++} + \text{CO}_3^{--}$ $K_{11} = 10^{-4.24}$ (reference 16).

^b K_2 calculated from the equilibrium constants for the reactions [1] and [11].

^c K_3 and K_{10} calculated using the calcium balance, ionic balance, K_1 and the following data: pH of saturated lime = 12.4 (reference 17), total solubility of lime in water = 2×10^{-2} mole/liter (reference 18).

An examination of the preceding equations shows that, when calcite approaches equilibrium with water at high pH values, an excess of the negative HCO_3^- and CO_3^{--} species will exist, whereas at low pH values an excess of the positive Ca^{++} , CaHCO_3^+ , and CaOH^+ species will occur. These ionic species may be produced at the solid-solution interface or may form in solution and subsequently adsorb on the mineral in amounts proportional to their concentrations in solution. The net result will be the same in either case: a positive charge on the surface at low pH or a negative charge at high pH. It is important to recognize that these two methods of surface charge generation are indistinguishable thermodynamically.

When the IEP and the ZPC are identical, the addition of solid to a solution at the pH corresponding to the IEP will cause no change in the solution pH, since equal amounts of H^+ and OH^- will be consumed to produce the species mentioned.

Besides the usual electrokinetic methods, the ZPC can be determined from the flotation response of the solid when treated with physically adsorbed anionic and cationic collectors. The physically adsorbed surfactants will adsorb strongly only when the surface is charged oppositely to the collector. This technique has been used before (19) and has been shown to correlate well

In this study, these three methods, electrokinetics, solution equilibrium, and flotation, have been used to determine the zero point of charge of calcite.

EXPERIMENTAL MATERIALS

Iceland Spar calcite was crushed in a mortar and pestle and sized. The 35/65 mesh size fraction used for the experiments was stored in conductivity water. All solutions were made with conductivity water that was prepared by passing distilled water through a demineralizing column and through a two-stage Heraeus quartz still. The water was used for experiments only if the conductivity was less than 7×10^{-7} $\text{ohm}^{-1} \text{cm}^{-1}$. It was stored in a stoppered Pyrex bottle. Since the water was used later for equilibration of the system in the presence of air, no attempt was made to keep air out of the bottle. Reagent grade nitric acid and sodium hydroxide were used for pH adjustments.

EXPERIMENTAL PROCEDURE

The reactions at the calcite-water interface were studied by measuring the ζ potential, the pH of the system, and the calcium and carbonate concentrations as functions of the equilibration time. The ζ potential was determined by the streaming potential technique.

The apparatus used for streaming po-

tential studies is based with some modifications on the same principles and assembly described earlier (20-22). Approximately 100 g. of calcite and 800 ml. of solution were used for each streaming experiment. The entire porous plug was made of 35/65 mesh calcite particles. An 80 mesh platinum wire gauze welded onto the electrode prevented the escape of any particles from the plug. An impedance bridge coupled to a decade capacitor was used for resistance measurements. The streaming potential E and the driving pressure P were simultaneously measured by the following method. As the solution flowed through the plug under pressure, a streaming potential was developed and was fed continuously into a vibrating reed electrometer and the output was recorded. The flow was suddenly stopped by turning a stopcock with one hand while at the same instant the pressure in the manometer was locked by turning by 45 degrees with the other hand a 3-way stopcock between the manometer and the streaming potential flask. The streaming potential at the instant flow stopped was read from the recording by noting the difference between the readings just before and after stopping the flow. The pressure at the instant when the flow stopped was read on the manometer. The operation was repeated several times in both directions of flow, and an average E/P was obtained. This method was much simpler than those used previously, since it was not necessary to maintain the driving pressure constant throughout the experiment. Also the effect of polarization on the streaming potential value obtained was eliminated.

The zeta potential of calcite was calculated using the formula (20, 21)

$$\zeta = [9.69 + 0.05(t-25)] \times 10^4 \frac{EA}{P} \text{ mv}$$

where t is the temperature of the solution in $^\circ\text{C}$, E is the streaming potential in volts, P is the driving pressure in centimeters of mercury, and γ is the specific conductivity of the solution in $\text{ohm}^{-1} \text{cm}^{-1}$.

The following procedure was used in the study of the rate of equilibration at the surface. After a plug of the mineral was

made, zeta potentials and pH were measured after streaming in each direction. The measurements were continued until there was no apparent change between successive readings. It was observed that, unlike the case of insoluble oxides and silicates, this system did not reach equilibrium by streaming the solution through the plug. Hence, the solution containing the mineral was transferred to a 1000 c.c. flask and mixed on a tumbler for several weeks. The zeta potential of the calcite, pH, and calcium and carbonate concentrations of the system were measured periodically. Mixing was continued until values of ζ and pH had remained constant for a period of at least two weeks. To obtain such an apparent equilibrium, it was often necessary to mix for nearly two months. Continuous mixing for longer times caused considerable formation of fines.

Calcium in solution was measured by atomic absorption. Total carbonate in solution was analyzed by mixing the solution with acid diluent and absorbing the released carbon dioxide in an alkaline solution containing phenolphthalein. The change in color of the solution was determined using an autoanalyzer at 550 μ .

Experiments were done in this manner with water adjusted to different initial pH values, as follows:

Experiment 1: no acid or alkali added—initial pH 5.6;

Experiment 2: alkali added to give an initial pH of 8.2;

Experiment 3: alkali added to give an initial pH of 9.9;

Experiment 4: alkali added to give an initial pH of 11.5;

Experiment 5: acid added to give an initial pH of 3.0;

Experiment 6: acid added to give an initial pH of 1.9.

Flotation experiments were made in a Hallimond cell (23, 24) with dodecylammonium acetate (DDA) as the cationic collector and dodecyl sulfate (DDSO₄) as the anionic collector. A 2-g. sample of the 35/65 mesh Iceland spar was conditioned for 10 min. with the required amount of acid or base; then the collector was added

and conditioned for 2 min. Nitrogen was bubbled through the cell at the rate of 30 ml./min. for 1 min., and the float and nonfloat portions were filtered, dried, and weighed.

RESULTS AND DISCUSSION

Zeta Potential. Figure 1 gives the zeta potential of calcite as a function of pH for various intervals of mixing the mineral with the solution. The closed circles in Fig. 1 give the values obtained for zeta potential after the solution had been streamed through the plug a number of times, but not mixed on the tumbler. On mixing the mineral with the solution on a tumbler, further changes in ζ and pH were observed and are shown by other curves in Fig. 1. It can be seen that streaming potential measurements gave an initial value of 10.8 for the ZPC. Equilibration on the tumbler shifted the ZPC to lower values. A final value of 9.5 was obtained for conditions under which there was no apparent change in pH of the solution on mixing for at least two weeks. The change of ζ is shown in Fig. 2. Zeta potential increased in magnitude both on the alkaline (experiment 4) and on the acid side (experiments 5, 6) of the ZPC. In the intermediate pH range, initially the behavior was similar to that of the alkaline range. All replications in these ranges showed the same changes. The ZPC ob-

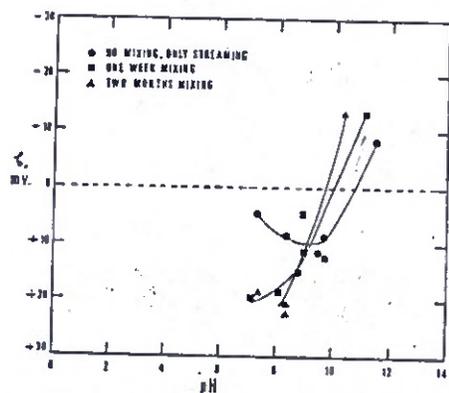


Fig. 1. Zeta potential of calcite in equilibrium with aqueous solutions and air as a function of pH and mixing.

tained from the ζ measurements may differ from the IEP if specific adsorption of any ion occurs. It can also be different if equilibrium has not yet been attained. If, as postulated subsequently, Ca^{++} and HCO_3^- are the principal potential-determining ions, then a ZPC higher than the IEP could be explained, because the calcium ion, being divalent, would be specifically adsorbed.

Solution Equilibrium IEP and Minimum Solubility. Figure 3 shows the changes in pH of the solutions, and Figs. 4 and 5 show the calcium and carbonate solubility as a function of mixing intervals. Most of the changes in pH of the solutions occurred immediately after calcite was added to the solution. Even the solution with an initial pH value as low as 1.9 gave a pH of 7.0 soon after coming in contact with the mineral. Addition of more acid to obtain data at still lower pH values was not done, since it would result in considerable dissolution of the calcite.

The pH of the solutions above 8.2 is found to decrease, whereas solutions below 8.2 increase with mixing time. A solution at pH 8.2 would undergo no net change in pH on equilibrating with the mineral. In other words, at this pH, equivalent amounts of hydrogen and hydroxyl are consumed by reactions such as hydrolysis of calcium and carbonate ions and adsorption at the mineral-solution interface. According to the definition given earlier, pH 8.2 is, therefore, the experimental isoelectric point of calcite. At pH values lower than the IEP, the solution will become more alkaline on addition of calcite, because of reactions [3] and [4] proceeding in the forward direction and reactions [8] and [9] in the reverse direction. At high pH values, the reverse is true, and the pH of the solution will decrease.

Garrels and Christ (1) have calculated the pH of water in equilibrium with calcite and air, and have arrived at pH 8.4, which agrees closely with the experimental value obtained here. At this pH they also calculated the total carbonate and calcium solubility to be 10^{-3} and $10^{-3.4}$ moles/l., respectively, which compares favorably with

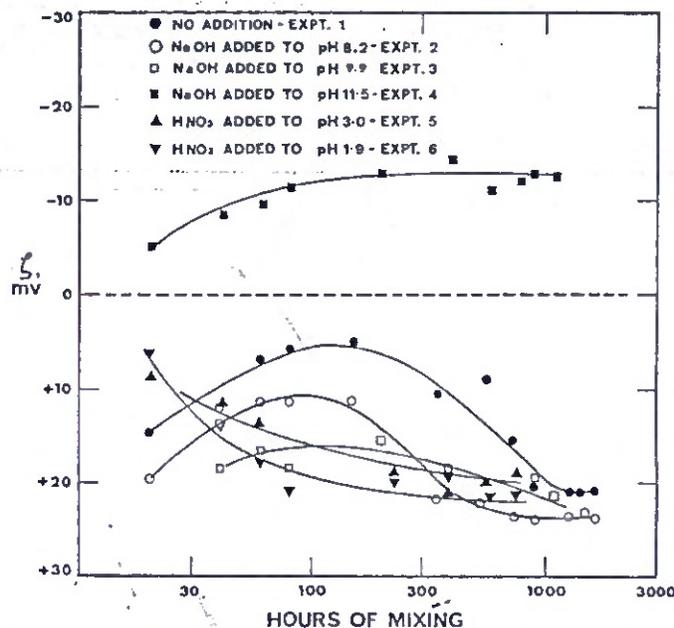


Fig. 2. Variation of zeta potential of calcite with mixing in aqueous solutions at different pH values

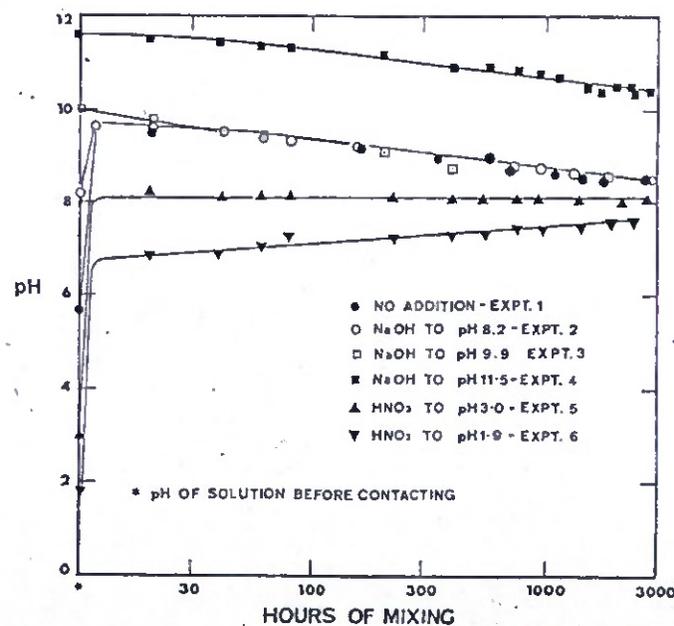


Fig. 3. Change in pH of the aqueous solutions with mixing in presence of calcite and air

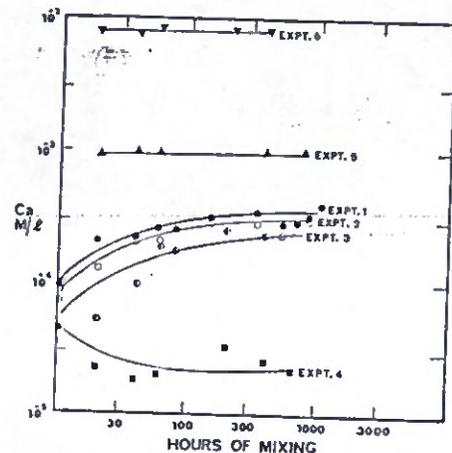


Fig. 4. Concentration of total calcium in the aqueous solutions in equilibrium with calcite and air, at different pH values.

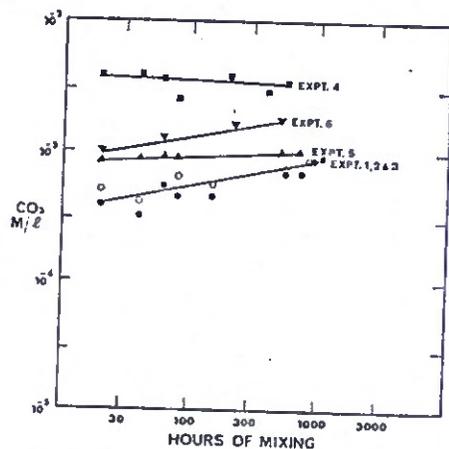


Fig. 5. Concentration of total carbonate in the aqueous solutions in equilibrium with calcite and air, at different pH values.

our experimental values of 10^{-3} and $10^{-3.4}$ moles/l.

We can evaluate the IEP from available thermodynamic data by calculating the concentrations of various species in equilibrium with calcite at different pH values, using the equilibrium constants given with Eqs. [1] to [10], and a carbon dioxide partial pressure of $10^{-2.5}$ atm. This method

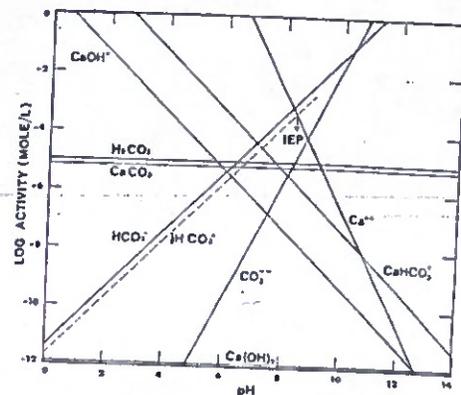


Fig. 6. Determination of isoelectric point and potential-determining ions for calcite-aqueous solution-air system using thermodynamic data.

of analysis, which has been used in similar systems (10, 25, 26), is illustrated in Fig. 6 and gives the IEP as pH 8.4. The figure also shows that HCO_3^- and Ca^{++} are the major surface potential-determining ions. Above pH 9 to 10, however, the CO_3^{--} ions also will have a major role in determining the potential of calcite. H^+ and OH^- ions are, of course, potential determining since they are in equilibrium with HCO_3^- , Ca^{++} , etc.

Beck (27) has shown that when a solution is in equilibrium with a solid phase, the IEP will correspond to the pH of minimum solubility. Since the isoelectric point is the condition at which the charges in the solution are equivalent electrically, it can be evaluated if the major species present in solution are known and if the concentrations of total dissolved species are measured. Figure 7 gives the measured values for total concentration of calcium and carbonate species in solution. Under equilibrium conditions the region of minimum total dissolved species is seen to be at pH 8 to 10; this confirms the value predicted in Fig. 7 and is comparable to the results obtained from pH measurements.

Flotation. The flotation results with collector concentrations of 1.6 and 3.3×10^{-5} moles/l. are shown in Fig. 8. Since the DDA floats the calcite only above pH 9, the surface must be negatively charged above this

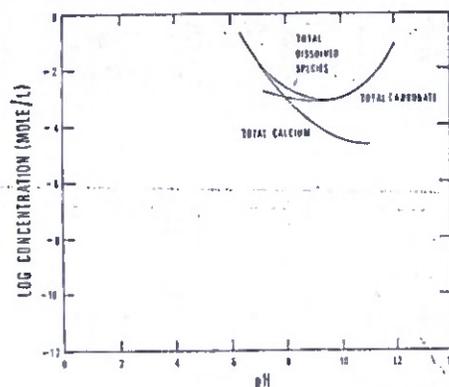


Fig. 7. Determination of isoelectric point from experimental measurements of total calcium and total carbonate concentrations in aqueous solutions in equilibrium with calcite and air.

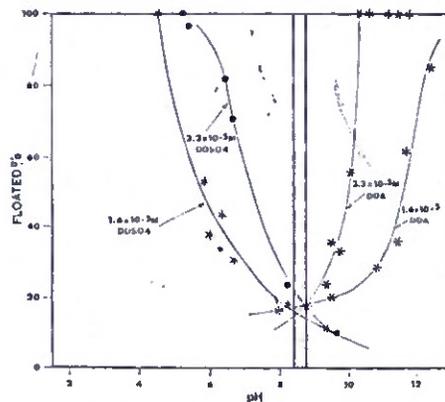


Fig. 8. Determination of zero point of charge from flotation of calcite with dodecylammonium acetate (DDA) and sodium dodecylsulfate (DDSO) solutions.

pH. Similarly, the DDSO_4 floats the calcite well only below pH 8, where the surface must have a positive charge. These measurements place the ZPC between pH 8 and 9.

Mechanism of Charge Generation. The surface $-\text{Ca}^+$ and $-\text{CO}_3^-$ ions can undergo hydrolysis according to Eqs. [3], [4], [8], and [9]. As mentioned earlier, at low pH values, reactions [3] and [4] will proceed in the forward direction and reactions [8] and [9] in the reverse direction, whereas at high pH values the reverse is true. This

differential hydrolysis will give rise to a net charge on the surface.

The continuous change in zeta potential and pH with mixing can be examined on the basis of the above mechanism for the charge development. It can be seen from Fig. 3 that the solutions in general showed a rapid increase in pH immediately on contacting the calcite, followed by a slow change over several weeks. This indicated that a mechanism involving a combination of fast and slow steps is responsible for the observed changes in the system. Such a possible mechanism is the hydrolysis of surface carbonate or calcium ions accompanied by the diffusion of hydrogen or hydroxyl ions through the double layer into or away from the interface. Thus in the experiments done with an acidic solution (experiments 5 and 6) the hydrolysis of surface carbonate ions



continues to take place making the mineral more positive and the solution more alkaline. Similarly, in the case of experiments done in the alkaline range (experiment 4), continued hydrolysis of calcium ions



is responsible for the observed change in ζ and pH of the solution with time. Here the surface becomes less positive and the pH of the solution decreases with time. That a diffusion-controlled process is important in the solubilization of calcite is supported by such works as that of Tate (28) in his recent chemical kinetic study of calcite-water system and that of Onoda and deBruyn (29) in which they proposed diffusion of protons through a hydrated gel-like interphase as the rate-controlling step in the equilibration of ferric oxide with aqueous solutions.

An alternate mechanism for calcite involves the dissolution of calcium and carbonate ions, followed by their hydrolysis into complexes in the solution; the complexes in turn adsorbing at the interface. The diffusion of the complexes to the interface might be the slow step in this case, resulting in the observed changes in ζ and pH with time. A slow preferential dis-

solution of calcium or carbonate ions, depending on the pH, as indicated by Figs. 4 and 5 could also result in the observed changes.

SUMMARY

1. The zero point of charge of calcite, as measured by the streaming potential technique, shifted gradually from an initial pH value of 10.8 towards 9.5 as equilibrium was approached. The isoelectric point of the solution, obtained from measurements of solution pH changes caused by the addition of calcite, is 8.2, in agreement with the value obtained graphically using thermodynamic data. The corresponding experimentally measured minimum of total species in solution lies between pH 8 and 10. Flotation experiments placed the ZPC between pH 8 and 9.

2. The principal potential-determining species are identified as Ca^{++} , HCO_3^- , H^+ , and OH^- . CO_3^{--} ions also have a major role above pH 9.

3. The principal mechanism of charge development at the surface is probably that of preferential hydrolysis of surface calcium and carbonate ions, or the hydrolysis of the bulk solution ions, followed by the adsorption of the resulting complexes at the surface. Gradual changes in zeta potential and pH of the system were observed for several days, indicating slow steps involved in the reactions developing the charge at the interface.

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Coagulation of Lyophobic Colloids by Metal Chelates. I¹

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The coagulation and reversal of charge of a silver bromide sol *in statu nascendi* by chelates has been studied as a function of pH. Ethylenediamine, propane-1,3-diamine, 2-picolyamine, 2,2'-dipyridyl, and 1,10-phenanthroline complexes of Ni(II) and Co(III) and ethylenediamine chromium(III) complex ions have been used in this work. The chelation of metal ions causes significant enhancement in their coagulation and reversal of charge abilities. These effects have been discussed in terms of the stability, size, and hydration of the chelate counterions.

INTRODUCTION

It appears that Freundlich (1) was the first to show that some monovalent large organic cations (strychnine, quinine, morphine, etc.) coagulate negative lyophobic colloids at concentrations considerably lower than simple inorganic ions of the same charge. More recently, this was confirmed for strychnine (2) and quinine (3). It was also shown that such cations can reverse the charge of the colloidal particles if added in sufficient concentrations. A review of the reversal of charge effects of such ions, containing a rather complete bibliography, has recently appeared (4). It is generally accepted that their enhanced coagulation activity and their ability to reverse the charge are due to stronger adsorption on lyophobic sol particles. For metal ions it was shown earlier that a great increase in adsorption is observed when these ions become hydrolyzed (4-6). There is also an indication that the size and the configuration of the coagulating ions affect their interaction with a colloidal particle. No previous studies contained sufficient information to correlate the charge, size, configuration, and chemical composition of a complex counterion with coagulation or stabilization properties.

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Metal chelates seem to be well suited for an investigation of these effects. With the use of the same central atom and different ligands, it is possible to prepare complex ions of the same charge but of various sizes and having different active groups. By replacing the central atom and using the same ligands, one can change the ionic charge keeping all other parameters essentially constant.

In addition to theoretical interest this work is of practical importance because it indicates the possibility of providing extremely efficient coagulating and/or stabilizing agents.

This first paper contains the results on the interaction of silver bromide sols with a number of nickel(II), cobalt(III), and chromium(III) chelates. It is shown that chelate complexes of these ions are much more efficient coagulating and stabilizing agents than the corresponding free central atoms. Indeed, the coagulation and reversal of charge concentrations of some of the nickel chelates investigated show that these complexes are more powerful coagulants than simple ions of +4 charge or even of any of the surface-active agents reported in the literature.

It should be mentioned that in recent years numerous studies have appeared in which fatty acids and other surface-active agents of various chain lengths were used as