by the degree of thermal aging of the melt. The decrease in the rate of gelation may be explained on the basis of dissolution of the smaller crystallites at elevated temperatures. At the time of casting, these crystallites are not present to serve as nuclei, and the rate of crystallization would be decreased. The crystallites reappear after an induction period at low temperatures. This may be demonstrated by storage of the thermally aged melt in a refrigerator for a period of time. Subsequent measurement of the tensile relaxation modulus of films cast from this melt show an increase in its value. This reversal of the thermal degradation of the melt lends support to the crystalline-amorphous concept.

Viscosity studies of the melt proved ineffectual in describing changes occurring in the tensile properties of films cast from the melt. Results indicated an orderly decrease in molecular weight with thermal aging. Changes in the tensile properties could not be reconciled with changes in molecular weight. Not only were these changes not parallel with the decrease in viscosity but also there was no way to explain the reversal of thermal changes during low temperature storage of the melt. Although some changes in the tensile properties may result from a scission of the polymer chain

during hydrolysis, it does not appear to be the major contributing factor.

To obtain a complete picture of the changes occurring in the rheological properties of gelatin films, it seems that, in addition to viscometric studies, one must measure some viscoelastic property whereby one may obtain information about the cross-linking processes occurring during gelation. It is felt that these changes may be responsible for some of the technological problems arising in the use of gelatin systems in the pharmaceutical industry.

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Powdered Particle Interactions: Suspension Flocculation and Caking III

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The chemistry of bismuth subnitrate in aqueous suspension has been investigated and explained in terms of coordination theory. Particular attention has been given to the reaction that occurs between phosphate ions and the surface of the bismuth subnitrate particles. Flocculation and caking phenomena are reviewed and interpreted in the light of these new findings.

IN A PREVIOUS paper (1) flocculation phenomena for bismuth subnitrate suspension systems were reported in terms of microscopic data and the relative suspension heights obtained from a series of controlled flocculation experiments. Strong bonds were seen to form between the particles while in the suspended state. The particles were held in fixed relative positions as they settled and were unable to shift and slide past one another to squeeze out the suspension medium and form a dense, compact sediment. Instead, the flocculated particles settled into the framework of a bulky sediment.

In this prior work (1) some effort was made to suggest the probable nature of the reacting

groups, but only tentative conclusions could be drawn. The work has continued with a closer inspection of the reactions of bismuth subnitrate in aqueous suspension in the hope that such information could provide a better insight into the mechanics of flocculation.

The literature (2-7) contains little detailed information on bismuth subnitrate or its reactions. A number of empirical formulas have been assigned to the compound. It is evident that the composition and properties of the crystalline material will vary, depending upon the method of preparation and the nature of changes that may occur when the material is subjected to further processing. The structure of the commercial product cannot be reduced to lattice formulas that describe an exact crystal geometry.

MATERIALS AND METHODS

Materials.—Bismuth subnitrate N.F. from the same lot, supplied by Mallinckrodt Chemical Works,

St. Louis, Mo., was used throughout the experiments. Monobasic potassium phosphate, reagent grade, supplied by Merck & Co., Rahway, N. J., was used in preparing the phosphate solutions. All other materials used were of reagent grade.

Equipment.—A Birrell wrist-action shaker, model DD, was used to agitate the bismuth subnitrate suspensions undergoing time reactions. Spectrophotometric determinations were made on a Coleman, Jr., spectrophotometer, model 6-A. A Beckman extended range pH meter was used to obtain the pH data.

Methods.—PHOSPHATE DETERMINATIONS.—The concentration of phosphate ion was determined through use of the molybdovanadophosphoric acid method, described by Boltz (8).

NITRATE DETERMINATIONS.—The concentration of nitrate ion was followed by the phenoldisulfonic acid method, described by Boltz (9).

EXPERIMENTAL WORK

Attention was first directed toward the reaction that occurs between phosphate ions and bismuth subnitrate in aqueous suspension. A series of solutions of known phosphate ion concentrations was prepared and used to obtain the upper curve of Fig. 1. The same solutions of phosphate ion were then used as the suspending media for a series of 2% bismuth subnitrate suspensions, and the lower curve was obtained. The downward shift in phosphate ion concentration was the result of its reaction with the bismuth subnitrate. If no reaction had taken place, the two curves would have been identical.

It was soon found that the amount of phosphate ion removed from the suspension medium varied with time. Three sets of a series of 100 ml. 2% bismuth subnitrate suspensions were prepared, with each set at a different level of initial phosphate ion concentration. The results are shown in Fig. 2, which plots the concentration of phosphate ion remaining in the suspension medium *versus* time. The results indicate that the uptake of phosphate

TIME, MIN.

Fig. 2.—A plot of the concentrations of phosphate ion remaining in 2% bismuth subnitrate suspensions *vs.* time from the moment of preparing the suspensions. The three curves present data from suspensions prepared at three different initial phosphate ion concentrations. The curves have been marked with these initial concentrations.

ion is independent of its initial concentration in the suspension medium, and that the rate at which reactive sites appear on the surfaces of the particles is the controlling factor. It should be noted that all three of the initial concentrations used were sufficient to cause the flocculation of the suspended particles. The amount of phosphate removed from the suspension medium has been calculated and plotted as one of the curves of Fig. 5.

It was found that the amount of phosphate ion required to cause flocculation increases as an aqueous bismuth subnitrate suspension is aged. For a 2% suspension, the requirement rose from 1.0×10^{-4} to 1.4×10^{-4} meq. phosphorus (as phosphate ion) per milliliter of suspension, during the first 15 minutes. No aging effect could be shown beyond this initial period of time by this technique.

Next, studies were conducted on the changes in pH that result from the suspension of bismuth subnitrate powder in water. The data could be converted to hydrogen ion concentration where this was of assistance in interpreting the phenomenon. The suspension medium under test was first adjusted to pH 7.00, and the bismuth subnitrate then added all at once in an amount calculated to give a 2% suspension. The data for bismuth subnitrate suspended in water have been plotted as one of the curves of Figs. 3 and 4. The same data were converted to milliequivalents of hydrogen ion released with time and plotted as one of the curves of Fig. 5.

Comparable pH *versus* time plots were obtained for 2% bismuth subnitrate suspensions containing different amounts of phosphate ion. The results are shown in Fig. 3. Buffering by the phosphate ion tended to shift the initial portion of the curves upward and to the right so that it was not clear whether the release of hydrogen ion was the same in each medium. The experiment was repeated using chloride ion as the flocculating agent. It showed an ability to flocculate comparable to that of phosphate ion, but no buffering effect was expected to cloud an analysis of the results. The data have been plotted in Fig. 4. As can be seen, the presence of chloride ion enhanced the initial release of hydrogen ions. However, the effect was short lived, for after the first 40 seconds the pH gradually rose, indicating the removal of hydrogen ions from the suspension medium. This response to the presence of chloride ion was particularly

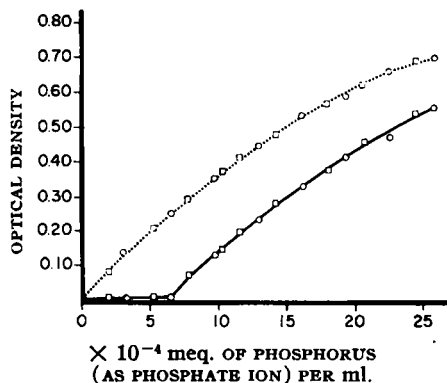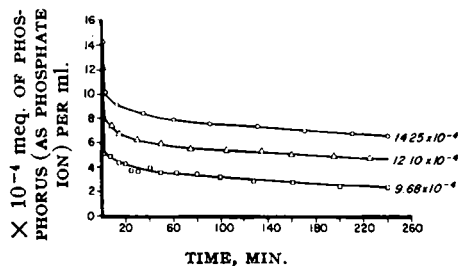X 10^{-4} meq. OF PHOSPHORUS (AS PHOSPHATE ION) PER ml.

Fig. 1.—A plot of optical density *vs.* phosphate ion concentration. The dotted line presents the data obtained from a series of solutions of known phosphate ion content. The solid line plots data on the concentration of phosphate ion remaining in the suspension media, after bismuth subnitrate 2% concentration was added to each of these known solutions. The experiment was duplicated, with one set of data shown as O and the other as □.
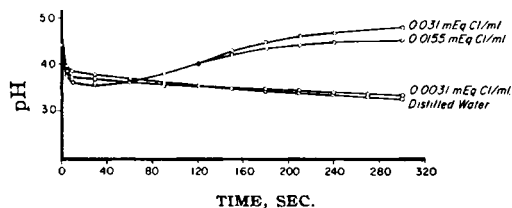
Fig. 3.—A plot of pH *vs.* time for freshly prepared bismuth subnitrate suspension systems. The bismuth subnitrate in dry powder form was added to solutions containing different concentrations of chloride ion to form a series of 2% suspensions. The chloride solutions were adjusted to pH 7.00 prior to the addition of the solid material. The curves have been marked to show the initial chloride ion concentrations, and are compared against the results obtained with distilled water.

marked when its concentration in the suspending medium was increased to over ten times the amount required to cause flocculation.

The concentration of nitrate ion in the bismuth subnitrate suspension medium also varied with time. The data have been plotted as one of the curves of Fig. 5. It can be seen that hydrogen ion is released in an amount almost double that of the nitrate ion, and thus the interaction of bismuth subnitrate with water is not one of simple hydrolysis to form nitric acid.

The final phase of the work was concerned with the disappearance of phosphate ion with time as a bismuth subnitrate suspension is aged. Reference to Fig. 5 will show that no 24-hour value has been given for the disappearance of phosphorus (as phosphate ion) from the suspension medium. This is because, at low levels of phosphate ion concentration, all of the ion disappeared from the suspension medium within the first 24 hours. After several trials, a 48-hour reading was obtained by raising the initial phosphate ion concentration to 200×10^{-4} meq. phosphorus (as phosphate ion) per ml. After 48 hours on the shaking machine, the pH was buffered at 4.05 by the phosphate remaining in solution, and 104×10^{-4} meq. of phosphorus (as phosphate ion) had been removed from each milliliter of the suspension medium. Nitric acid was then added to bring the pH down to 3.0 and the suspension shaken for another 48 hours. There was no further uptake of phosphate ion. The pH was reduced to 1.5, and all of the remaining phosphate ion was removed from the suspension medium during an additional 48 hours of shaking.

DISCUSSION OF RESULTS

The empirical formulas that have been assigned to bismuth subnitrate may be representative of the bulk substance of the crystal or powder, but do not necessarily provide an adequate description of the crystal surface. As a crystal forms, its surface is an amorphous, hydrated, electrostatically charged region of transition between the mother liquor and the fully formed crystalline material. Dean (10) suggests this for a colloid such as α-Fe$_2$O$_3$, in which the iron and oxygen atoms in the surface region may either be thought of as adsorbed ions, or as atoms belonging to the crystal structure but having unsatisfied valence and coordination bonds

which are in interaction with the molecules of the solution.

In commercial processes, it seems the pH generally rises as the bismuth subnitrate is formed. Thus the surface composition of the crystal would be strongly influenced by the final pH of the precipitation medium and this effect would be further accentuated by the loss of nitric acid that occurs during the washing step. The drying step also acts upon the surface, rather than the bulk substance of the crystal. Adsorbed water molecules are driven off
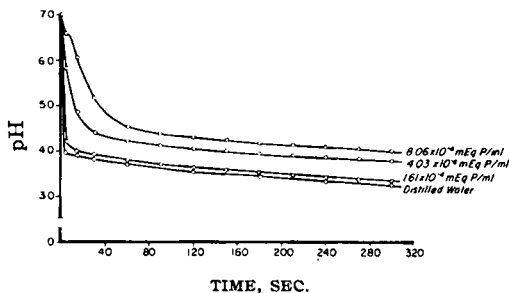

Fig. 4.—A plot of pH *vs.* time for freshly prepared bismuth subnitrate suspension systems. The bismuth subnitrate in dry powder form was added to solutions containing different concentrations of phosphate ion to form a series of 2% suspensions. The phosphate solutions were adjusted to pH 7.00 prior to the addition of the solid material. The curves have been marked to show the initial phosphate ion concentrations and are compared against the results obtained with distilled water.

and hydroxy groups at the surface are converted to oxy bridges.

The reactions of bismuth subnitrate can be understood within the framework of Werner's coordination theory (11). Dean (10) has discussed coordination theory pictorially in terms of the ferric ion. The water molecules of a coordination shell are held so strongly that the bonds between the iron atom and the oxygen atoms of the water molecules resemble covalent bonds. Two electrons from the oxygen atom serve to hold the water to the charged metallic atom and are drawn toward the metal atom so that the bonds between the hydrogen atoms and the oxygen are weakened. The hydrated ion becomes acidic and yields hydrogen ions to the solution.

These concepts can be extended to the bismuth subnitrate suspension system. When bismuth subnitrate forms a 2% suspension in water, nitrate ions appear in the suspension medium, and the pH falls from 7.00 to 3.95. These facts have been summarized in Fig. 5. Utilizing coordination theory, the reaction sequence shown in Fig. 6 (reactions *a* through *e*) is proposed.

In these reaction steps, the bismuth atom has been assigned a coordination number of 8. This finds justification in the crystal structure of the compound, bismuth oxychloride. Wells (12) and Hückel (13) have both discussed the layered structure of the BiOCl crystal, in which the bismuth atom has been shown to be 8-coordinated. Very similar formulas could be drawn if it should later be shown that the bismuth atom in bismuth subnitrate is 6-coordinated.

The data plotted in Fig. 3 show the change in

pH that takes place when bismuth subnitrate is added to a neutral solution of sodium chloride. There is a rapid release of hydrogen ion, just as is seen when bismuth subnitrate is added to water, but the release is enhanced by the presence of the chloride ion. We believe this may be a case in which the solubility of a very slightly soluble substance is increased by the presence of other ions (14). The nitrate concentration is in a range where the Debye-Hückel effect would be of significance.

As nitrate ions leave the crystal surface, unsatisfied bismuth sites would become available for covalent-type bonding with water of coordination. As the covalent-type bonds are formed, hydrogen ions are released to the suspension medium, and the pH falls. Figure 3 also shows a pH reversal effect, due to the presence of chloride ion. This seems due to the insolubility of bismuth oxychloride or its precursors and to the high electronegativity of the chloride atom. By forming a Bi-Cl bond having more of an ionic than covalent character,
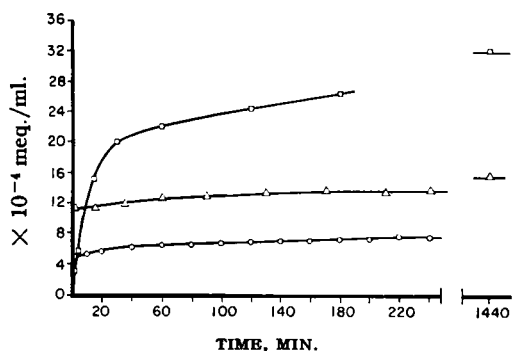
Fig. 5.—A summary plot showing ion concentrations *vs.* time. The data was obtained from several different suspension systems. Key: □, the curve on hydrogen ion concentration *vs.* time when bismuth subnitrate is added in dry powder form to give an aqueous 2% bismuth subnitrate suspension; △, the curve on nitrate ion concentration *vs.* time when bismuth subnitrate is added in dry powder form to give an aqueous 2% bismuth subnitrate suspension; ○, the curve on loss of phosphate ion concentration *vs.* time, following the addition of bismuth subnitrate in dry powder form to a solution containing monobasic potassium phosphate.

the strength of the covalent-type bonds between the bismuth atom and its water of coordination is diminished. With a weakening of these bonds, the oxygen atoms of the water of coordination become correspondingly more negative, and there is some recall of the hydrogen ions previously released. The net effect is a rise in the pH of the solution. The change in pH with time, when bismuth subnitrate is added to water containing the phosphate ion, has been shown in Fig. 4. Buffering is one reason for the difference in response to phosphate or chloride ion, but another factor is that the phosphate group is not so electronegative as is the chlorine atom. The significant pH reversal seen with chloride ion would thus not be expected from the medium containing the phosphate ion.

The aging of a bismuth subnitrate suspension can be partly understood in terms of reactions *a* through *e* in Fig. 6. Figure 5 shows that the nitrate

and hydrogen ion concentrations of the suspension medium increase rapidly following the addition of the bismuth subnitrate, and the concentrations of both ions asymptotically approach equilibrium levels. As aging proceeds, respective sites appear due to the ionization of the nitrate group. However, this ionization accounts for but a part of the reactive sites that ultimately appear on the crystal surface. The particle surface reactivity increases to such an extent that the phosphate ion concentration will drop from 200×10^{-4} to 96×10^{-4} meq. of phosphorus (as phosphate ion) per milliliter, over a 48-hour period. The exact reason for this increase in the number of reactive sites is unknown. It is assumed that it is the end result of an opening of oxy bridges as the crystal surface becomes increasingly hydrated.

As evidence of the change in surface charge and reactivity with time, it is of interest to consider the deflocculation of a phosphate ion flocculated bismuth subnitrate suspension. If such a suspension is freshly formed and continuously shaken while it ages, it will revert to the deflocculated state. The shaking action tends to separate the flocculated particles while their surface is being altered by the hydration mechanism. A positive particle surface
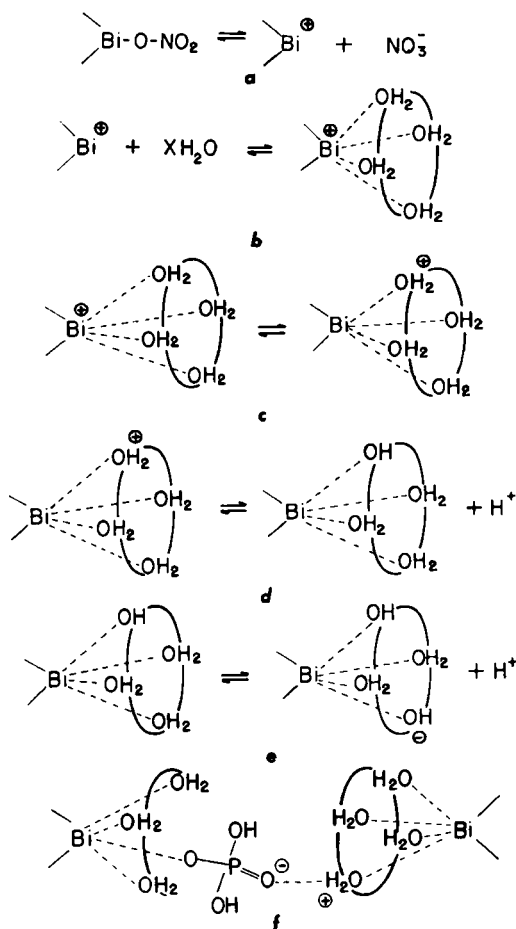
COVALENT-TYPE BONDING   HYDROGEN BONDING

Fig. 6.—Proposed reaction sequence utilizing the coordination theory.

charge would result, and there may be a further reduction in the negativity of the surface as reacted phosphate groups form second bonds with the crystal surface when adjacent bismuth sites become available. This type of reaction at the crystal surface may be inferred from the crystal structure of a salt such as aluminum phosphate (15).

Thus, aging processes combined with vigorous agitation will cause the flocculated system to revert to a deflocculated state in which the individual particles have a net positive surface charge. In the absence of shaking, there is no apparent tendency to deflocculate on aging for a period of several months. However, if a suspension flocculated by a small amount of phosphate ion is allowed to age for several months and then shaken, it will promptly deflocculate. It should be noted that the hydration phenomenon does not cause an increase in the amount of phosphate ion required to cause flocculation of the system. Also, the deflocculated system may be reflocculated by the addition of a relatively small amount of phosphate ion. It is not necessary to add phosphate ion in an amount sufficient to satisfy all of the reactive sites on the aged crystal surfaces. This serves to reinforce the thought that only a few phosphate bridges are required to bond the bismuth subnitrate particles into a floc.

Where an excess of phosphate ion is present and the pH is held at a relatively high level, as was the case when the suspension medium initially contained 200×10^{-4} meq. of phosphorus (as phosphate ion) per milliliter, the suspension remains in the flocculated state throughout the aging process. Shaking is instrumental in breaking the larger flocs into smaller aggregates, but there is no reversion to the completely deflocculated suspension that might be expected. The reversal of charge (irregular series) for iron oxide particles suspended in water has been discussed by Van Wazer (16). The particles initially carry a positive charge and will be flocculated by the addition of polyphosphate ions. However, if more polyphosphate is introduced into the system, there is a reversal of particle charge, and the system reverts to the deflocculated state. In the case of bismuth subnitrate, this type of deflocculation was not seen despite the vigorous shaking action to which the suspension was subjected.

From the above, it appears that the surface charge on the bismuth subnitrate macroparticles was not so effective in preventing flocculation or in causing deflocculation as the surface charge in a typical colloidal system. This finding emphasizes the difference between a colloidal and noncolloidal suspension system. For the noncolloidal bismuth subnitrate, flocculation phenomena must be explained in terms of the number of bonds formed between the particles and in terms of the strengths of such bonds. The chemistry of the ferric ion and of the bismuth subnitrate crystal surface point to at least two types of bonds. These are illustrated in reaction f of Fig. 6. This bonding mechanism would imply that the nitrate ion could be responsible for the flocculation of a bismuth subnitrate suspension. Indeed this is the case, for a degree of flocculation is seen when a concentrated solution of potassium nitrate is added to a bismuth subnitrate suspension.

One other phenomenon remains to be considered. When a bismuth subnitrate suspension was flocculated with a large excess of phosphate ion, a little more than half of the phosphate was removed from the suspension medium as the suspension was aged with shaking for a 48-hour period. The balance of the phosphate could be removed by adjusting the pH to 1.5 and continuing the shaking process. This seems due to the action of the acid upon those groups in the crystal surface which were formed later in the manufacturing process. Reactive sites appear in large number as the crystal surface is etched by the acid.

SUMMARY

The surface chemistry of bismuth subnitrate particles in aqueous suspension has been discussed in terms of Werner's coordination theory. This new approach to the chemistry of bismuth subnitrate has been of value in explaining the phenomena associated with bismuth subnitrate suspensions. Data are reported which support the application of the theory to this special case involving a suspended solid. Aging phenomena have also been reported for the bismuth subnitrate suspension system.

Coordination theory has been used in a further discussion of the nature of the bonds that exist between the particles of a phosphate ion flocculated bismuth subnitrate suspension. An important difference between colloidal and noncolloidal systems is based on this point. To bond noncolloidal particles, relatively strong bonds must be present in sufficient number over those areas of particle surface that come in contact with each other. As particle size decreases, fewer bonds or bonds of a weaker nature, can serve to bind the particles together into a floc.

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