

- (119) Banes, D., *ibid.*, **46**, 601(1957).
 (120) Hayden, A. L., Ford, L. A., and Houk, A. E. H., *ibid.*, **47**, 157(1958).
 (121) Lindblad, C. G., and Ågren, A., *Farm. Revy*, **53**, 69(1954).
 (122) Büchi, J., and Huber, R., *Pharm. Acta Helv.*, **36**, 571(1961).
 (123) Lach, J. L., Patel, D. M., and Blaug, S. M., *THIS JOURNAL*, **45**, 611(1956).
 (124) Yeh, S.-Y., and Lach, J. L., *ibid.*, **50**, 30(1961).
 (125) Welsh, L. H., *ibid.*, **44**, 507(1955).
 (126) Higuchi, T., Sokolowski, T. D., and Schroeter, L. C., *ibid.*, **48**, 553(1959).
 (127) Jermstad, A., and Jensen, K. B., *Pharm. Acta Helv.*, **26**, 33(1951).
 (128) Levine, J., and Horrocks, E., *J. Assoc. Offic. Agr. Chemists*, **43**, 233(1960).
 (129) Schill, G., and Ågren, A., *Svensk Farm. Tidskr.*, **56**, 55(1952).
 (130) Haddock, L. A., and Evers, N., *Quart. J. Pharm. Pharmacol.*, **4**, 314(1931).
 (131) Levine, J., *J. Assoc. Offic. Agr. Chemists*, **46**, 641(1963).
 (132) *Ibid.*, **44**, 285(1961).
 (133) Miller, D. J., *ibid.*, **41**, 490(1958).
 (134) *Ibid.*, **42**, 455(1959).
 (135) Levine, J., *ibid.*, **45**, 595(1962).
 (136) Levine, J., and Ottes, R. T., *ibid.*, **44**, 291(1961).
 (137) "United States Pharmacopeia," 16th rev., Mack Publishing Co., Easton, Pa., 1960, p. 933.
 (138) Theivagt, J. G., and Campbell, D. J., *Anal. Chem.*, **31**, 1375(1959).
 (139) Murray, T. K., *ibid.*, **34**, 1241(1962).
 (140) Higuchi, T., Patel, T. K., Bonow, E. R., and Landsman, J., *THIS JOURNAL*, **41**, 293(1952).
 (141) Perlmutter, S. H., *J. Assoc. Offic. Agr. Chemists*, **43**, 282(1960).
 (142) *Ibid.*, **44**, 312(1961).
 (143) Levine, J., and Hohmann, J., to be published.
 (144) de Ropp, R. S., *THIS JOURNAL*, **49**, 756(1960).
 (145) Schwartz, M. A., Kuramoto, R., and Malspeis, L., *ibid.*, **45**, 814(1956).
 (146) Taraszka, A. J., and Marcus, A. D., *ibid.*, **47**, 99(1958).
 (147) Clark, W., personal communication.
 (148) "United States Pharmacopeia," 16th rev., Mack Publishing Co., Easton, Pa., 1960, pp. 223-226.
 (149) *Op. cit.*, pp. 482-484.
 (150) Banes, D., and Houk, A. E. H., unpublished.
 (151) "1st Supplement to the United States Pharmacopeia," 16th rev., 1962, p. 16.
 (152) "National Formulary," 11th ed., J. B. Lippincott Co., Philadelphia, Pa., 1960, pp. 13-14.
 (153) "Official Methods of Analysis," 9th ed., Association of Official Agricultural Chemists, Washington, D. C., 1960, sections 32.052-32.056, p. 473.
 (154) Alexander, T. G., *J. Assoc. Offic. Agr. Chemists*, **43**, 224(1960).
 (155) "Official Methods of Analysis," 9th ed., Association of Official Agricultural Chemists, Washington, D. C., 1960, sections 32.075-32.080, p. 477.
 (156) *J. Assoc. Offic. Agr. Chemists*, **45**, 214(1962).
 (157) "Official Methods of Analysis," 9th ed., Association of Official Agricultural Chemists, Washington, D. C., 1960 section 32.090, p. 480.
 (158) *Op. cit.*, sections 32.164-32.169, p. 496.
 (159) *Op. cit.*, sections 32.309-32.314, p. 532.
 (160) Welsh, L. H., *J. Assoc. Offic. Agr. Chemists*, **30**, 639(1956).
 (161) "Official Methods of Analysis," 9th ed., Association of Official Agricultural Chemists, Washington, D. C., 1960, sections 32.327-32.330, p. 535.
 (162) Smith, G., *J. Assoc. Offic. Agr. Chemists*, **41**, 55, 499(1958).
 (163) "Official Methods of Analysis," 9th ed., Association of Official Agricultural Chemists, Washington, D. C., 1960, sections 32.355-32.360, p. 540.
 (164) Banes, D., *J. Assoc. Offic. Agr. Chemists*, **41**, 56, 487(1958).
 (165) *Ibid.*, **44**, 149(1961).
 (166) *Ibid.*, **44**, 153(1961).
 (167) *Ibid.*, **44**, 317(1961).
 (168) *Ibid.*, **44**, 152(1961).
 (169) *Ibid.*, **46**, 148(1963).

Research Articles

Powdered Particle Interactions: Suspension Flocculation and Caking II

By BERNARD ECANOW and ROBERT G. WILSON

The flocculation of a bismuth subnitrate suspension has been explained as principally due to forces other than van der Waals acting between the suspended particles. Two basic types of bonds are described. The conclusions are supported by microscopic data and by data on relative suspension heights obtained from a series of controlled flocculation experiments. These findings disagree with a proposed concept, which views the flocculation of a bismuth subnitrate suspension as the end result of the action of van der Waals forces, following the neutralization of the zeta potential of the suspended particles.

IN THE INITIAL paper of this series (1), a 2% sulfamerazine suspension was chosen for a study of the phenomena of flocculation and of caking. Particles of sulfamerazine were suspended in dilute dioctyl sodium sulfosuccinate solution, and either aluminum or ferric ions were introduced as the flocculating agent. It was shown that flocculation was influenced both by wetting agent concentration and by the chemical

Received June 19, 1962, from the College of Pharmacy, University of Illinois, Chicago.

Accepted for publication April 10, 1963.

Abstracted from a thesis submitted by Robert G. Wilson to the Graduate School, University of Illinois at the Medical Center, Chicago, in partial fulfillment of Doctor of Philosophy degree requirements.

reaction that took place between the above trivalent cations and the anions of the wetting agent. Where the chemical reaction was a dominant factor in flocculation, the mechanics were visualized as the adsorption of wetting agent anions on the surface of the sulfamerazine particles, followed by a chemical coprecipitation between the flocculating agent cations and the adsorbed anions. An analogous reaction is obtained when common soaps react with the heavy metal ions in "hard" water.

The sulfamerazine suspension system was previously discussed in the literature (2, 3).

It had been suggested that the flocculation was due to the interaction of the van der Waals forces operating after the zeta potential of the particles had been neutralized by the flocculating agent. This proposal was questioned on two counts (1): (a) The particles were in macro-particulate suspension, rather than in colloidal dispersion. Van der Waals forces, although presumably present, have not been shown to be of significance in the type of system studied, where particles are above the colloidal size range. (b) The flocculation was virtually immediate, on mixing, and thus was more typical of a chemical reaction than of the reaction rate associated with the action of van der Waals forces. Burton (4) has shown that the coagulation of a colloidal system, following the neutralization of particle charge, is a slow process which depends upon the Brownian movement of the particles.

A bismuth subnitrate suspension which could be flocculated by the addition of monobasic potassium phosphate solution was also reported in the literature (2, 3). The flocculation reaction was discussed in terms of zeta potential and van der Waals forces. This again raised the above questions relative to particle size and speed of the flocculation reaction. The bismuth subnitrate-monobasic potassium phosphate suspension system has in this report been considered from a different viewpoint, with the thought that both flocculation and caking phenomena might be explained on some basis other than that previously proposed.

In the exploratory work, a 2% bismuth subnitrate suspension was reacted with a flocculating agent, and the degree of flocculation was judged empirically from the settling rate. This could be done, since flocculated particles settle more rapidly than do the same particles in a deflocculated state. The words, "flocculated" and "deflocculated," are here used in accordance with the definition given by Fischer and Gans in their chapter in Alexander (5). The following compounds, at a concentration of 1 mmole of phosphate per 100 ml. of suspension, were tested for their flocculating ability.

Flocculating Agent	Relative pH of the Additive in Solution	Flocculating Action
Tri-sodium phosphate	12.0	little
Dibasic sodium phosphate	8.7	little
Monobasic sodium phosphate	4.3	marked
Phosphoric acid	2.2	marked

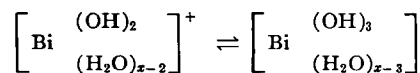
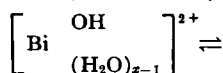
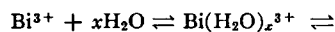
As can be seen, there was little flocculating action for additive solutions of high pH, but a marked degree of flocculation at lower levels of pH. Since the same concentration of phosphate was present in each case, it seemed that flocculation was pH-dependent. This finding lent credence to the thought that a chemical reaction might be involved.

Bismuth subnitrate for pharmaceutical use is a white, slightly hygroscopic powder. Under the microscope, the powder can be resolved to transparent, orthorhombic crystals averaging 10 to 15 μ in size. The compound may be produced by several quite comparable processes. Perhaps the simplest is to prepare a solution of bismuth nitrate in nitric acid solution of the proper strength and to then pour this solution into a large quantity of water. The bismuth nitrate promptly hydrolyzes, precipitating bismuth subnitrate from an acid medium. Nitric acid is a product of the hydrolysis reaction as well as being present in the initial bismuth nitrate solution. The precipitated bismuth subnitrate is separated by filtration or centrifugation, is carefully dried, and is sold in this form. Because of the conditions of the process, bismuth subnitrate resuspends in water to give a slightly acid medium. An alternate production method (6) is to add sodium carbonate to bismuth nitrate in acid solution until the pH rises to 5.0. At this point, the precipitated bismuth subnitrate is separated and carefully dried as before. Both of the methods discussed will give bismuth subnitrates of variable composition, and the pH obtained on resuspending the solid will be influenced both by the manufacturing process and by the extent to which the material was dried.

Hückel (7) has discussed the "iso-poly bases" at some length. These are compounds which are known to form a variety of weakly basic hydroxides. The hydrolysis of an iso-poly base leads to a hydrated oxide of the compound, or to an oxide complexed with an indeterminate number of water molecules. The composition and structure of the hydroxide, as well as its initial formation, are all strongly pH dependent. Hückel has also said that the size of the iso-poly cations formed can be strongly influenced by the types of anions present in the precipitation medium. The attainment of the hydrolysis equilibrium is described as a slow process, and one in which the initial reversible equilibrium reaction is frequently followed by an irreversible aging process. Because various products may be formed at the different stages of the reaction, and because these products may then be taken to different stages of the aging process, it follows that the end result of the hydrolysis reaction is a product which is variable and complex in its composition.

Hückel did not specifically deal with bismuth subnitrate. However, a footnote in his work indicates that the hydrolysis reactions of the bismuth salts are thought to be comparable to those of trivalent chromium. Utilizing Hückel's presentation, but substituting trivalent bismuth for chromium, the following outlines some of the typical reactions of an iso-poly base.

(a) The formation of "aquo-cations."¹



¹ As in Hückel's work, bonding lines are not drawn in the illustrated compounds.

accord. After the suspension heights had been recorded, the pH of each suspension medium was taken on a Beckman pH meter (glass electrode model H2), and the data were correlated with the suspension heights.

RESULTS

The bismuth subnitrate used in this series of experiments was found to suspend in water to give a pH of 3.05. A milky, uniform suspension was obtained, from which the bismuth subnitrate

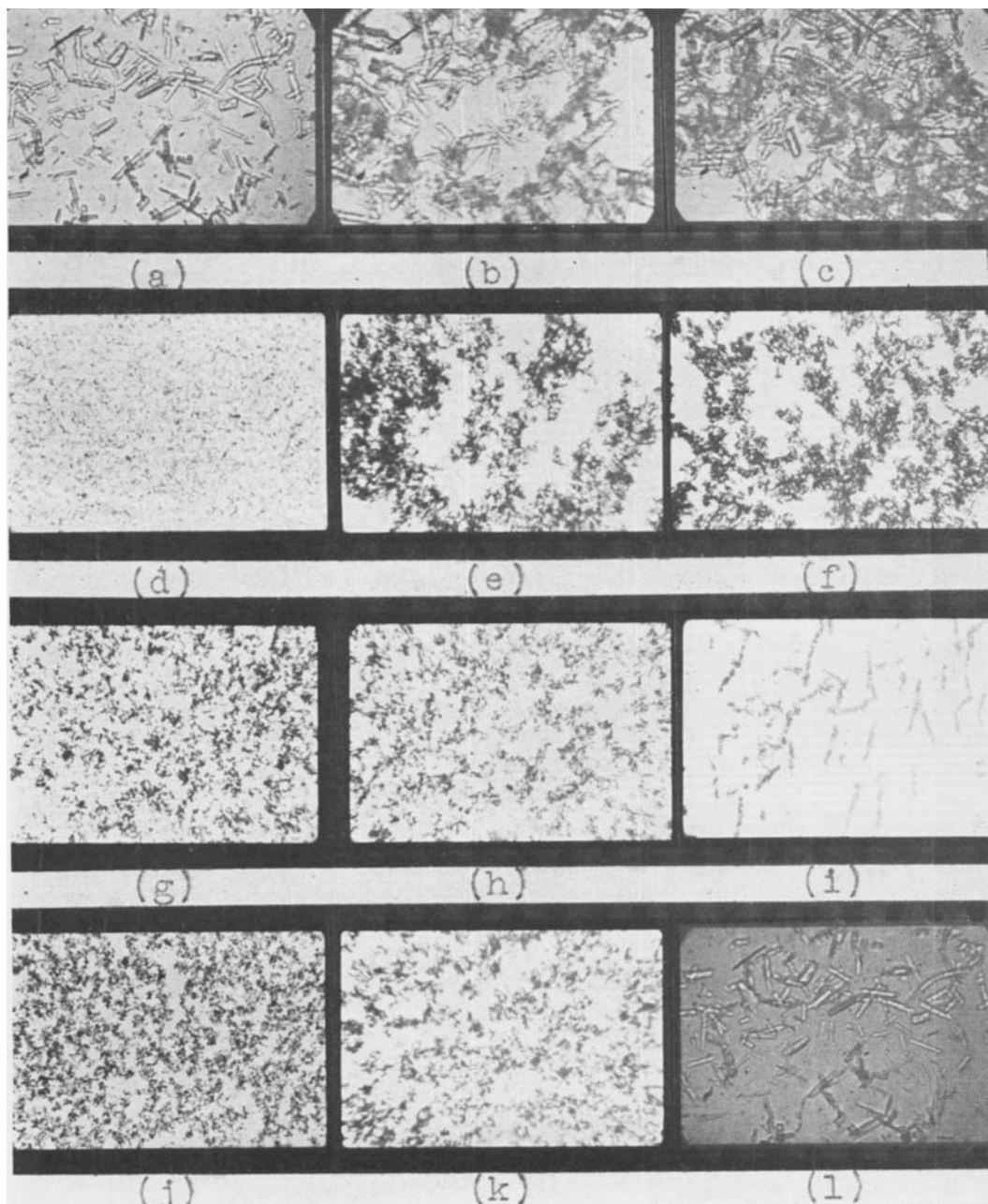


Fig. 1.—Key: (a) bismuth subnitrate in water (oil immersion); (b) bismuth subnitrate-flocculated (oil immersion); (c) bismuth subnitrate-flocculated (oil immersion); (d) bismuth subnitrate in water (low magnification); (e) bismuth subnitrate in nitric acid solution-pH 0.46 (low magnification); (f) bismuth subnitrate in phosphoric acid solution-pH 0.94 (low magnification); (g) bismuth subnitrate in trisodium phosphate solution (low magnification); (h) bismuth subnitrate with trisodium phosphate in nitric acid solution-pH 1.13 (low magnification); (i) bismuth subnitrate with trisodium phosphate in nitric acid solution-pH 0.86 (low magnification); (j) bismuth subnitrate with sodium citrate in nitric acid solution-pH 1.73 (low magnification); (k) bismuth subnitrate with sodium citrate in nitric acid solution-pH 0.65 (low magnification); (l) bismuth subnitrate in water (oil immersion). All suspensions were shaken vigorously prior to sampling.

particles slowly settled to form a dense precipitate. The supernatant liquid took several days to clear, which is indicative of the slowness of the settling rate. After all of the suspension had settled, the cylindrical graduate could be inverted, with the precipitate holding its shape and position at the bottom of the graduate. However, it was possible to resuspend the material easily if the compact precipitate was mechanically disrupted before the mixture was shaken. The appearance of the bismuth subnitrate crystals, microscopically, is shown in Fig. 1*a, d, and l*.

In the initial group of tests, various amounts of 7% nitric acid solution were added to a series of 10% bismuth subnitrate suspensions. The results are shown in Fig. 3. The bismuth subnitrate flocculated, and its relative suspension height more than doubled as the pH dropped below 1.0. A microscopic study showed that the individual bismuth subnitrate crystals were clumped into loose aggregates. Figure 1*e* compares the flocculated material against the original finely-divided suspension of crystals. The aggregates had a rapid settling rate and settled to leave a clear solution. It was found that the increase in suspension height was due to the voids between and within the aggregates as they slowly settled to form the precipitate. When the cylindrical graduate was carefully inverted, the precipitated material tended to hold its shape. In other words, there was some resistance to sediment flow under these conditions. The flocculated material could easily be resuspended by shaking. It should be emphasized, though, that the resuspended material was still in the aggregated condition and could not be shaken back to indi-

vidual crystals, such as those seen in the untreated bismuth subnitrate suspension. To continue with this portion of the experimental work, it seemed of interest to study the acid-base response of the flocculation mechanism. Since the degree of flocculation was increased by hydrogen ion concentration, could the response be reversed by hydroxyl ions? A bismuth subnitrate suspension was treated with nitric acid until the pH had been reduced to approximately 0.8. The acid was then back-titrated with potassium hydroxide solution. A slight decrease in suspension height was seen, but certainly not a return to the original level. Whatever the changes induced by acid, it seemed they could not be reversed by a simple change in the pH.

Next, experiments were run in which the pH was followed as acids were added to bismuth subnitrate suspensions. Normal acid-base type neutralization curves might logically be expected, but this was not the

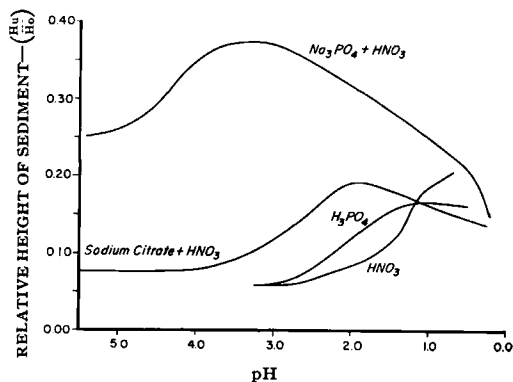


Fig. 2.—Composite plot of relative height of sediment vs. pH, demonstrating the relative activity of several flocculating agents.

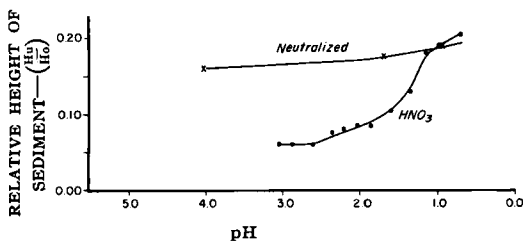


Fig. 3.—Relative height of sediment vs. pH for a bismuth subnitrate suspension flocculated by nitric acid. The acid was then neutralized with dilute potassium hydroxide solution.

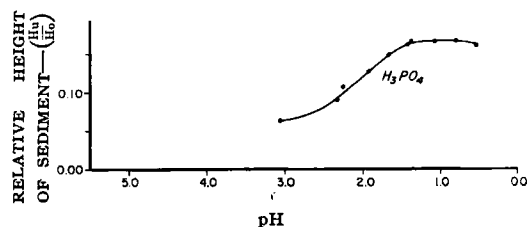


Fig. 4.—Relative height of sediment vs. pH for a bismuth subnitrate suspension flocculated by phosphoric acid.

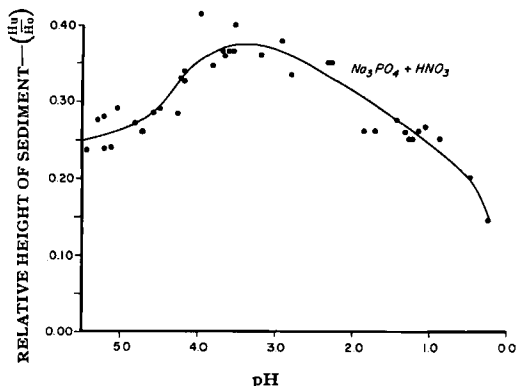


Fig. 5.—Relative height of sediment vs. pH for a bismuth subnitrate suspension flocculated by trisodium phosphate (4.72% w/v) and various amounts of nitric acid.

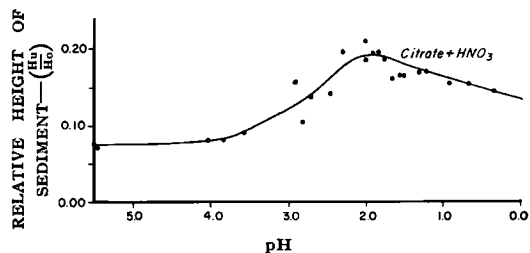


Fig. 6.—Relative height of sediment vs. pH for a bismuth subnitrate suspension flocculated by sodium citrate (9.80% w/v) and various amounts of nitric acid.

case. Titration of a 10% bismuth subnitrate suspension with either nitric acid or phosphoric acid gave a pH curve that was virtually identical with the pH curve obtained by titrating distilled water, if the distilled water was first adjusted to the initial pH of the bismuth subnitrate suspension. Although it is known that bismuth subnitrate will dissolve in strong mineral acids, quite concentrated acids are required. The pH must be well below 0.5 before a significant degree of dissolution is seen. The above observations suggested the existence of crystal surface changes as the result of the decrease in pH level. An equilibrium reaction appeared to be involved.

Figure 3 demonstrates the flocculation response as nitric acid was added to a bismuth subnitrate suspension. As the pH decreased, the relative suspension height showed a marked increase. The test was rerun, using phosphoric acid as the additive. Figure 4 gives the results of this test series, and it is apparent that the response was very similar to that obtained with nitric acid. The photographs of Fig. 1*d*, *e*, and *f* serve to illustrate the change that takes place as these acids are added. As hydrogen ion concentration increases, the individual crystals tend to clump together; the clumps act to give a bulkier, more readily resuspendable precipitate. In the lower pH range, the sediment would hold its shape when the graduate was cautiously inverted. This resistance to flow was more marked for the phosphoric acid series than for the nitric acid series. A definite "form" or "structure" was present, and it would have been possible to describe the sediment as a "soft cake." This correlates with the comments of Haines and Martin (2, 3). Simple shaking sufficed to resuspend the material.

The action of phosphate ion was further investigated through the addition of an excess of trisodium phosphate to a series of 10% bismuth subnitrate suspensions. Varying amounts of nitric acid were added, and data on relative suspension height *versus* pH were obtained and plotted as in Fig. 5. At all of the pH levels shown the relative suspension height was three or more times the height of the untreated material, and there was a maximum response between the pH levels 3.0 and 4.0. The flocculated material could easily be resuspended by shaking. However, here again, there was some evidence of a "structure" within the sediment. The experiment was run again, but sodium citrate was used in place of the trisodium phosphate. The results were somewhat comparable, as shown in Fig. 6. However, marked flocculation was not obtained until the pH had dropped below 3.0. The maximum fell between pH 1.5 and 2.5, and the relative suspension height decreased as pH decreased below 1.5. Microscopic studies on the test groups gave the typical photographs shown in Fig. 1. The graphical results have been summarized in the composite plot of Fig. 2.

DISCUSSION

Bismuth subnitrate is a crystalline material, occurring as transparent, elongated orthorhombic particles. Since the crystals themselves were identical in microscopic appearance throughout the course of each experiment, the variation in degree of flocculation must be because of differences in the composition of the molecular layers at the surface of the crystals. A crystal surface may vary in both

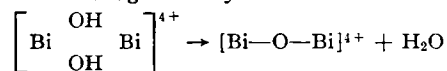
the magnitude and sign of its electrostatic charges depending on the nature of the chemical groups residing in, or projecting from, its surface layer. The characteristics of the bismuth subnitrate crystal surface are influenced by the previous history of the crystal and by the chemical environment into which the crystal is placed.

The concept of a bonding between crystal surfaces is also required for an explanation of the experimental results. Such an attraction would be the end product of crystal surface conditions and could involve such things as electrostatic bonding, hydrogen bonding, or perhaps even van der Waals forces. When flocculating agents are present and the bismuth subnitrate crystals approach closely to one another, there is an attraction which culminates in a bonding of one crystal to the other. The bonding forces appear strong enough to hold the crystals in fixed relative positions during normal, undisturbed settling, but are weak enough to allow agitation to break the sediment into clumps of crystals, or for gentle vibration to reduce the relative suspension height by causing the suspension to settle more than it would under gravitational effects alone.

If one of the flocculated suspensions is shaken vigorously, the bismuth subnitrate is resuspended. However, it is not resuspended in the form of the individual crystals, but instead in the form of clumps of crystals, such as have been shown in our photographs taken through the microscope. The size of the clumps is determined by the force of the agitation used in resuspending the material, and by the number and strength of the bonding forces between the crystal surfaces. An additional factor is the variation in the density of the clumps. Our photographic work demonstrates an increase in density as the strength of the flocculating agent increases. The change in the density of the aggregates corresponds to an increase in the number or strength of bonds between the crystals.

In light of the above, the phenomenon of flocculation for a bismuth subnitrate suspension may be discussed as follows.

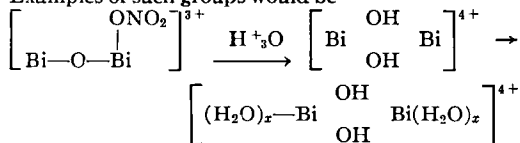
(a) When bismuth subnitrate crystals are produced, it appears that they have relatively few reactive points on their surfaces. It is presumed that the drying step tends to "seal in" some of the potentially active sites, as for example by the dehydration of "ol" bridges to "oxy" links.



The drying step would leave the surface with fewer "ol" groups. As a result, the particles in suspension would have less tendency to clump, would settle independently under the influence of gravity, and would be piled randomly on top of each other in the sediment. As settling continues, the crystals would tend to realign themselves, filling the void spaces and bringing large areas of the crystal surfaces into close proximity with each other. After standing for several days, the bismuth subnitrate precipitate has the ability to retain its shape when the container is inverted. However, vigorous shaking, plus some mechanical dislodging of the sediment, will promptly resuspend the individual crystals. This may be viewed as a sediment in which there are bonds between the crystals, but in which the

bonds are relatively weak and few in number. They are effective in giving "form" or "structure" to the sediment, only because of the close contact between relatively large areas of the crystal surfaces. When the particles are in suspension, the bonding forces are so weak and few in number that they are ineffective in holding the crystals together.

(b) When nitric or phosphoric acid is added to a bismuth subnitrate suspension, reactive groups of various kinds will be formed on the crystal surfaces. Examples of such groups would be

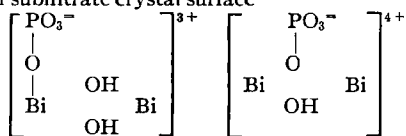


The higher the concentration of hydronium ion as flocculating agent, the greater the number of potential bonding sites that come into existence; thus the stronger is the total potential for forces of attraction and of bonding.

As small amounts of flocculating agents are introduced, there is a very loose clumping of the crystals in suspension. As these settle, the total effect of the bonding forces is weak enough to allow the crystals some freedom to realign themselves and thus to reduce the size of the voids in the sediment. However, the forces are active enough to prevent the complete realignment that was seen in the untreated bismuth subnitrate sediment.

At higher levels of flocculating agent, more and more bonding sites are created on the crystal surfaces. Their cumulative effect is strong enough to attract and bond tightly the individual crystals into compact, closely knit aggregates. When these aggregates settle, the crystals tend to be held in fixed relative positions and are thus unable to realign themselves to fill the voids in the sediment. Since the voids are present, the relative suspension height is correspondingly increased.

(c) The final system considered was that in which phosphate or citrate ions were introduced prior to the addition of the acid. Both anions give a somewhat similar response, so the discussion will be limited to the flocculating ability of the phosphate ion. Trisodium phosphate will react with the bismuth subnitrate crystal surface



As has been said, some "ol" bridges and positive charges are present on the original crystal surface. It is for this reason that flocculation may be obtained at pH levels above the initial pH of the bismuth subnitrate suspension. In this region, however, there are relatively few of these "ol" bridges available for reaction, and the crystals tend to clump into very loose masses. As acid is added to this system, "oxy" links are converted to "ol" bridges and nitrate groups leave the crystal surface as ions. Additional bonding sites are thus formed.

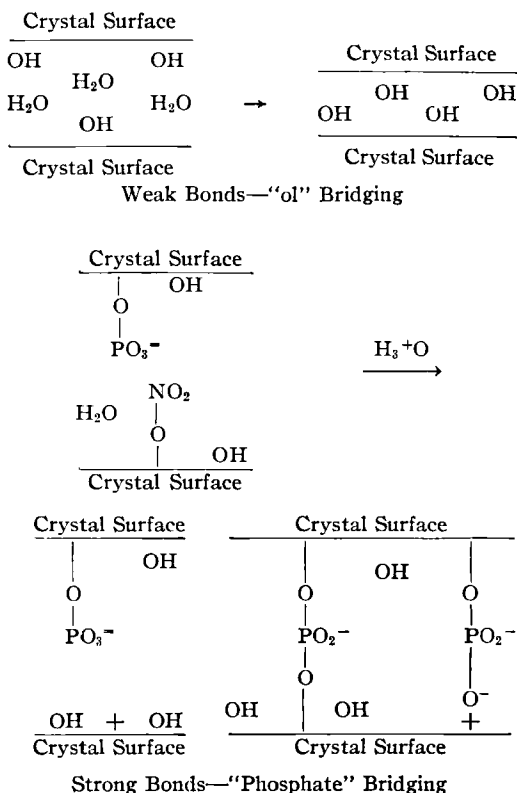
The additional sites and the relatively high strength of the bonding forces developed by the presence of the phosphate groups give the loose, lacy clumps of bismuth subnitrate crystals a high degree of structural form. When they settle in the

form of a precipitate, a vast amount of void space is enclosed. The sediment bulks to the unexpectedly large relative suspension heights noted between pH 3.0 and 2.0. As more and more acid is added, the number of bonding sites is increased, and the attractive forces tend to draw the crystals into clumps that are increasingly compact. The compactness eliminates the voids, and when the clumps settle, they enclose less void space even though their structural framework may be stronger than that obtained at the higher levels of pH. Thus the relative suspension height drops off from the maximum level and approaches the value given by the simple addition of phosphoric acid to a bismuth subnitrate suspension.

It should be emphasized that the response to the addition of phosphoric acid is different than that obtained when trisodium phosphate is added and followed by nitric acid. The fundamental difference lies in the characteristics of the clumps of crystals that are formed. In the phosphoric acid series, the crystals clump into relatively tight masses right from the start, and the compactness increases as additional acid is added. With trisodium phosphate, the initial clumping is very loose and does not become compact until sufficient nitric acid has been added to drop the pH below 2.0.

CONCLUSIONS

The flocculation of a bismuth subnitrate suspension has been explained in terms of a crystal surface phenomenon—one in which there is a mutual interaction between crystals that culminates in a bonding of one crystal to another. Two types of bonds seem to be the chief contributors, and these can be described on the basis of their relative strengths



The weaker bonds are present to some extent in the original suspension, and the number of such bonds that can be formed increases as the concentration of hydrogen ion is increased. The stronger bonds are formed in the presence of phosphate ions, and again the number of potential bonds increases as the pH falls. An increase in hydrogen ion concentration tends to open additional reactive sites on the crystal surface.

The bonding between crystals gives rise to a clumping of crystals. As the clumps settle in the suspension medium, voids are formed both within and between the clumps. The differences in relative suspension height, from one system to the next, are a function of the number and size of the void spaces trapped within the sediment.

Where the bonds are weak and relatively few in number, a flocculated system fails to develop. The crystals sediment without the formation of voids, and the relative suspension height is at a low value. However, within the compacted sediment, the few weak bonds are able to exert sufficient bonding power to give the sediment some structural properties. Thus it shows some resistance to resuspension.

As the number of weak bonds increases, their total strength becomes sufficient to bond the crystals into a flocculated system. The crystals, although bound together, are able to adjust their relative positions as the precipitate settles. During this readjustment, the voids are decreased in size and an intermediate suspension height is obtained.

With a further increase in the number of weak bonds, the floc becomes quite compact. The bound crystals are capable of bridging the voids and of retaining them within the sediment. At this point, for the system involving weak inter-crystalline bonds, the relative suspension height reaches a maximum.

Where the bonds are strong but relatively few in number, as when sodium triphosphate is added to a bismuth subnitrate suspension, flocculation is seen. The floc settles, and the crystals are able to shift somewhat to eliminate a portion of the void space. However, a significant amount of void space is retained, and the sediment bulks to a substantial degree.

As more flocculating agent is added to form the stronger bonds, the density of the clumps increases slightly, but more importantly, the rigidity of the floc is increased. Thus when the material sediments, it is able to retain the voids and bulks to an extremely high relative suspension height.

SUMMARY

The bismuth subnitrate crystal surface is not easily described through structural formulas. It is a highly solvated, three-dimensional complex involving hydrogen bonds, hydroxy links, ionic charges, and electrostatic bonds. The diagrams contained in this report should be considered as suggestive of the actual condition of the crystal

surface rather than restrictive on the reader's concept of such a surface. Attention has been directed toward specific, isolated groups that are believed to be present.

When bismuth subnitrate is suspended in water, the crystal surface assumes a net positive charge because of the presence of ionic bismuth charges at the highly solvated surface. As phosphate is added to such a system, it reacts with both the "ol" groups and the available bismuth charges, first neutralizing the surface charge and then continuing to react further as more phosphate is added, until the surface charge has been reversed by a preponderance of phosphate ions bound to the surface. This concept finds support in the caking diagram of Martin (9), in which it was shown that the surface charge of suspended deflocculated bismuth subnitrate particles could be reversed by adding monobasic potassium phosphate to a suspension of bismuth subnitrate. The electrophoretic data was obtained in terms of particle movement, but was converted to zeta potential values when the caking diagram was drawn. Although zeta potential is a valid concept, its use in this situation tends to cloud the fact that the phosphate ions are reacting with the crystal surface—not gathering as an ionic atmosphere to shield the underlying charge on the particle surface.

A neutralization and reversal of net surface charge by chemical reaction of phosphate ions with the bismuth subnitrate crystal surface is the basic factor in the flocculation reaction under consideration in this report. It is important to recognize that a neutralization of net surface charge would yield a particle surface having "ol" groups, sites of positive charge, and sites of negative charge. The particle will not respond to electrophoresis at such an isoelectric point (a point at which there is a balance between negative and positive surface charges on the bismuth subnitrate particle). But if two crystal surfaces should come into close contact with each other, even at the isoelectric point, there would be ample opportunity for chemical or electrostatic interactions to occur between the surfaces and to end with the bonding of the two crystals in a flocculent state.

REFERENCES

- (1) Wilson, R. G., and Ecanow, B., *THIS JOURNAL*, **52**, 757(1963).
- (2) Haines, B. A., Jr., and Martin, A. N., *ibid.*, **50**, 228 (1961).
- (3) *Ibid.*, **50**, 753(1961).
- (4) Abramson, H. A., "Electrokinetic Phenomena and Their Application to Medicine," Chemical Catalog Co., Inc., New York, N. Y., 1934, p. 74.
- (5) Alexander, J., "Colloid Chemistry, Theoretical and Applied," Vol. VI, Reinhold Publishing Co., New York, N. Y., 1946, pp. 286-287.
- (6) Kirk, R. E., and Othmer, D. F., "Encyclopedia of Chemical Technology," Vol. 2, The Interscience Encyclopedia, Inc., New York, N. Y., 1954, p. 535.
- (7) Hüchel, W., "Structural Chemistry of Inorganic Compounds," Vol. 1, Elsevier Publishing Co., Inc., Amsterdam, The Netherlands, 1950, pp. 230-236.
- (8) Ward, H. T., and Kammermeyer, K., *Ind. Eng. Chem.*, **32**, 622(1940).
- (9) Martin, A. N., *THIS JOURNAL*, **50**, 513(1961).