Thus, the postulate that the bismuth polymer is a fragment of the bismuth–oxygen sheets no longer seems tenable, since it does not offer an easy mechanism by which a discrete polymer could be stabilized. The stability of a "hexamer" (or pentamer) over a wide range of conditions implies that it has a unique, presumably closed, structure and further aggregation cannot occur without a large change in free energy. It is unfortunate that the structure of bismuth oxyperchlorate is not known. One might expect the structure of this salt to be related to the structure of the polymeric ion in perchlorate solutions. These structures presumably would differ from the layer lattices found for the bismuth oxyhalides.

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[CONTRIBUTION FROM THE GRASSELLI CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Magnesium Polymetaphosphate

BY R. PFANSTIEL AND R. K. ILER

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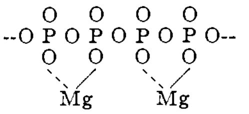
Hydrated magnesium polymetaphosphate prepared from non-cross-linked potassium polymetaphosphate is a viscous water-immiscible liquid which appears to be a coacervate. Since the hydrated polymer is a fluid rather than a gel, it is presumably not cross-linked; the divalent magnesium ions may therefore be chelated along the metaphosphate chain rather than bridged between chains. Upon being dried at 110° to the composition $[Mg(PO_3)_2 \cdot 2H_2O]_n$, the composition reverted to a brittle, white, opaque solid which is probably crosslinked by coördination of magnesium ions with the oxygen ions of adjacent polymetaphosphate chains.

It is the purpose of this paper to call attention to the unusual behavior of hydrated magnesium polymetaphosphate. When formed in aqueous solution, this inorganic polymer separates as a heavy viscous water-immiscible liquid containing about 60% water and 40% $[(Mg(PO_3)_2)_n]$. This liquid phase appears to be a coacervate. H. G. Bungenberg de Jong[1] has pointed out that coacervation, or the precipitation of a second liquid phase, is a behavior which is typical of linear macromolecular colloids of the highly viscous type.

It is postulated that the magnesium ions are firmly bound to the polymetaphosphate chains by chelation



thus producing an essentially non-ionic linear polymer. Such molecules probably tend to coil up and also to associate with each other and, as stated by Bungenberg de Jong, "in the coacervate there are mutually associated macromolecules which penetrate each other at any rate with their peripheral loops." The amount of water in the coacervate, 15 molecules per $Mg(PO_3)_2$ unit, is probably about sufficient to complete the coördination sphere of the magnesium and to form a single hydrogen-bonded layer of water molecules about the polymer chain. The tendency of a hydrophilic colloid particle to bind water at least to the extent of a monomolecular layer has been pointed out recently by Dalton and Iler.[2] The coacervate phase of magnesium polymetaphosphate may therefore be pictured as a tangled skein of thread-like hydrated magnesium polymetaphosphate molecules.

Pure hydrated magnesium polymetaphosphate has not been described previously in the literature. The fact that alkali metal polymetaphosphates are precipitated when calcium or barium salts are added in sufficient quantity to be equivalent to about two-thirds of the alkali metal ion content, has been pointed out by Karbe and Jander.[3] Precipitation of alkali metal polymetaphosphate by magnesium and other divalent ions as gummy or oily precipitates is described by Thilo, Schulz and Wichmann.[4]

Experimental

Magnesium chloride will precipitate the corresponding polymetaphosphate from a solution of KPO_3 when a stoichiometric quantity of the salt is added. When a non-cross-linked KPO_3[5] is used, this initial rubbery precipitate, which still contains some alkali metal ions, can be dissolved by stirring in cold water. Since more than half of the cations in this product are divalent, yet the polymer is not cross-linked since it is still water soluble, it is concluded that the divalent ions must be chelated to the polymer chains. The introduction of a small amount of a trivalent cation such as aluminum, gives a rubbery, insoluble, obviously cross-linked product. An insoluble product also is obtained from KPO_3 which is cross-linked through a deficiency of K in the melt.

If the above redissolved magnesium–sodium–potassium polymetaphosphate is again precipitated with an excess of magnesium salt, the product is at first a rubbery mass, having the mechanical characteristics of a partially cross-linked gel. It is possible that as the last of the sodium and potassium ions are removed, adjacent metaphosphate units may not be available for chelation, so that the magnesium ions then cause cross-linking. However, the fresh precipitate, which resembles art gum, becomes less rigid after a few hours and is transformed into a very viscous taffy-like mass which can be pulled out into thin threads and is thus apparently no longer cross-linked. It is postulated that there is a rearranging of the chelate groups to permit the magnesium ions, which are initially present as cross-links between adjacent chains, to migrate to suitable positions for chelation. This seems reasonable, since it might be expected that the chelate structure would be the more stable arrangement. The stability of the magnesium

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[1] H. G. Bungenberg de Jong, H. R. Kruyt, ed., "Colloid Science," II, Elsevier Publishing Co., Inc., New York, N. Y., 1949, p. 232.

[2] R. L. Dalton and R. K. Iler, *J. Phys. Chem.*, **60**, 955 (1956).

[3] V. K. Karbe and G. Jander, *Kolloid Beihefte*, **54**, 9, 105 (1943).

[4] V. E. Thilo, G. Schulz and E.-M. Wichmann, *Z. anorg. Chem.*, **271-273**, 182 (1953).

[5] R. Pfanstiel and R. K. Iler, THIS JOURNAL, **74**, 6059 (1952).

complex may be indicated by the equilibrium constant for the equation

$$M^{+2} + P_4O_{12}^{-4} = MP_4O_{12}^{-2}$$

reported by Jones and Monk as being of the order of 7×10^{-6}, based on conductivity data at 25°,[6] where $K = [(M^{+2})(P_4O_{12}^{-4})]/MP_4O_{12}^{-2}$.

The non-cross-linked hydrated magnesium polymetaphosphate, when free from alkali metal ions, is only slightly soluble in water. In aqueous suspension it is a very viscous water-immiscible fluid. This is converted to a brittle solid when water is removed by drying in air or by washing with alcohol. It is postulated that when water is removed, the magnesium ions then coördinate with the oxygen of adjacent metaphosphate chains, giving a product which is highly cross-linked through coördination. Magnesium atoms may therefore act as cross-linking units when the metaphosphate is dry, but may not cause cross-linking when the structure is fully hydrated.

Preparation.—One-half gram mole (59 g.) of finely ground non-cross-linked KPO_3 and 413 g. of commercial sodium salt of "Dowex" 50 cation exchange resin were slurried together in 2441 g. of distilled water (always CO_2-free) for 25 minutes, keeping the *p*H of the slurry between 8 and 9 with small additions of dilute NaOH. The viscous solution was separated from the resin by suction through a glass wool pad.

To 2181 g. of this 0.2 *m* solution of Na, K, PO_3 was slowly added, with vigorous agitation, the stoichiometric amount of $MgCl_2 \cdot 6H_2O$ (44.2 g.) dissolved in 1000 ml. of distilled water, adjusted to *p*H 8.5 with MgO powder. The white rubbery precipitate was collected, squeezed to remove occluded solution, and slightly washed. It was then dissolved in 3000 ml. of distilled water by stirring and macerating the gum. The solution was adjusted to *p*H 8 with MgO powder, and was slowly added to a strongly agitated solution of 177 g. of $MgCl_2 \cdot 6H_2O$ in 1000 ml. of distilled water adjusted to *p*H 8.5 with MgO powder. The precipitated gum, now very soft and sticky, was transferred to a solution of 44 g. of $MgCl_2 \cdot 6H_2O$ in 1000 ml. of distilled water, adjusted to *p*H 9 with MgO, and the solution stirred over the precipitate for 16 hours. The viscous, extremely sticky and gummy oil was lightly washed, and then 400 ml. of distilled water (CO_2-free) adjusted to *p*H 8.5 with MgO, was stirred over it for 2 hours; yield of oil, 95 g. A small portion was dried to a film; the remainder was covered with distilled water, adjusted to *p*H 9.6 with MgO, and stored at 10°.

Composition of the air-dried film was as follows: Mg, 9.16, 9.46%; P, 23.04, 23.04%; K, 0.04%; Na, 0.00%; Cl, 0.29, 0.19%. Correcting for the magnesium chloride, Mg/P = 0.511; by difference, the water content was 31.7%. When dried at 110° at 10 mm. pressure, the film was very brittle and the water content was 16%, corresponding to $[Mg(PO_3)_2 \cdot 2H_2O]_n$. This composition suggests a cross-linked structure in which each Mg ion is coördinated with four oxygen atoms, two from each of two adjacent $(PO_3^-)_n$ chains, plus two molecules of water, to give a total of six oxygens surrounding the metal atom. This white opaque solid reverts to the viscous liquid state after prolonged soaking in water at room temperature. The liquid product stored at 10° underwent some hydrolysis in eight months, the *p*H having dropped from 9.6 to 6.0. Samples containing alkali metal ions seemed to be less stable.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Cysteine Complexes with the Cobalt(III) Ion. III. The Role of Gaseous Oxygen in the Formation of Cysteine Complexes of Cobalt(III) from Cobalt(II) Ion and Cysteine

BY ROY G. NEVILLE[1,2]

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The amounts of gaseous oxygen absorbed by cysteine solutions containing various concentrations of cobalt(II) ion have been studied. In dilute solution, with cobalt to cysteine ratios of 1:3 or more, one atom of cobalt was equivalent to 0.75 atom of oxygen; at ratios less than 1:3, one molecule of cysteine was equivalent to 0.25 atom of oxygen. In all experiments varying amounts of cystine were formed, and the oxidation reaction was not stoichiometrically pure. In concentrated solution, the formation of the bis- and red tris-cysteinates of cobalt(III), from cobalt(II) ion and cysteine at appropriate *p*H, proceeds with the absorption of 0.5 atom of oxygen per atom of cobalt. This corresponds exactly with the conversion of cobalt from the (II) to the (III) state, and excludes the formulation of these complexes as disulfide structures.

In entire absence of gaseous oxygen, Michaelis[3] showed that a mixture of cobalt(II) ion and cysteine at *p*H 7–8 gave a cobalt(II) complex "usually slightly olive-green" but pink in the presence of a large excess of cysteine. The cobalt(II) complex was very rapidly oxidized by gaseous oxygen to an intensely dark brown complex which was shown by Schubert[4] to be cobalt(III) bis-cysteinate. Michaelis and co-workers[3,5] and Kendall and Holst[6] reported that during this reaction one atom of oxygen was taken up. The oxidation reaction was not simple, since Kendall and Holst showed that about 23% of cystine was simultaneously formed. This amount of oxygen corresponds to two-thirds the amount necessary to oxidize the cysteine to cystine, or double the amount required to oxidize cobalt(II) to cobalt(III).

In a study of the oxidation of cobalt(II) bis-thioglycolate, Michaelis and Schubert[7] found that one-quarter of a mole of oxygen was absorbed per mole of cobalt. This observation was interpreted as corresponding either to the oxidation of cobalt(II) to cobalt(III), or to the oxidation of sulfhydryl to disulfide. Cryoscopic measurements on the oxidized complex showed it to be dimeric, and a binucleate structure was accordingly assigned. However, the structure of the oxidized complex could not be considered as definitely established, and Michaelis suggested the possibility of a desmotropic relationship between the cobalt(III)–sulfhydryl and the cobalt(II)–disulfide structures.

Since the difficulties of assigning a precise structure in the case of the bis-thioglycolate apply equally to the case of the oxidized cysteine complexes of cobalt, it was considered desirable to in-

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(2) Abstracted from part of the Ph.D. thesis of Roy G. Neville.

(3) L. Michaelis and E. S. G. Barron, *J. Biol. Chem.*, **83**, 191 (1929).

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