Summary

This study was an exploratory one to survey the possibilities of ammonia for refining. Persons familiar with cottonseed oil refining recognize that techniques with respect to temperature, concentration, stirring rates, and the like, have an enormous influence on results. It is believed from this study that gaseous ammonia refining could be developed to equal or surpass present "two-step" processes. "Two-step" processes used for cottonseed oil refining all suffer from the need to re-refine with strong caustic to remove color. If an alternate color removal step is ever developed, gaseous ammonia refining might become a leading process. It is one of the least expensive raw materials. Furthermore, the ammonia could be recovered as such or sold as by-product ammonium sulfate resulting from acidulation of ammonium soapstocks.

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Iron Sequestration by Polyphosphates

R. R. IRANI and W. W. MORGENTHALER, Research Department, Inorganic Chemicals Division, Monsanto Chemical Co., St. Louis, Missouri

Abstract

The equilibrium sequestration of ferric and ferrous iron by polyphosphates has been measured at room temperature in the pH range of 4–11. In general, sequestration decreases with increase in pH or increase in the chain length of the polyphosphate. The dissociation constants of ferric pyrophosphate and ferric tripolyphosphate have been estimated to be around 10^{-23}. The polyphosphates form weaker ferrous complexes.

Introduction

SEQUESTRATION is the formation of soluble complexes of metal ions in the presence of other chemicals that would normally precipitate the metal ion. The chemicals that are capable of interacting with metal ions in this fashion are known as sequestering agents or sequestrants.

Sodium polyphosphates are the most widely used commercial sequestrants. In previous articles (3–5) the sequestration of calcium and magnesium by the polyphosphates was quantified. This article includes information on ferrous and ferric complexing by sodium polyphosphates, as well as an estimation of the dissociation constants of the complexes formed. Previous work in this area has been sketchy and has combined sequestration with the ability of polyphosphates to peptize iron hydroxide precipitates.

Experimental Procedure

Materials. Since commercial polyphosphates differ in composition, only purified and well-defined materials were used in this study. Crystalline tetrasodium pyrophosphate decahydrate and pentasodium tripolyphosphate hexahydrate (7) were used as sources for $Na_4P_2O_7$ and $Na_5P_3O_{10}$, respectively. The three anhydrous long chain sodium polyphosphates were characterized by their Na_2O/P_2O_5 ratios of 1.34, 1.15, and 1.033, indicating along with end-group titrations average chain lengths of 6, 14, and 60 phosphorus atoms per molecule, respectively. Other chemicals were C.P. grade.

Procedure. The developed procedure was found to be applicable to ferrous as well as ferric sequestration measurements. An aliquot volume of acidic iron chloride solution containing 2.5% iron was pipetted into a beaker and about 150 cc of distilled water was added along with aqueous sodium hydroxide to give the desired pH. The slurry was agitated for 20 min prior to addition of an aliquot of 2.5% stock sodium polyphosphate solution. After further pH adjustment, the solution was shaken on a wrist-action shaker for 48 hr to reach equilibrium. To coagulate colloidal iron hydroxides, the equilibrated mixture was centrifuged for 90 min at 23,000 g's in a Lourde centrifuge, refrigerated to maintain the temperature at 25 ± 1C. The supernatant solution was filtered and an aliquot was taken for iron determination. With ferrous iron, de-aerated water was used throughout to prohibit excessive oxidation.

Iron Determination. It was found that X-ray fluorescence is a convenient and precise method to measure either ferrous or ferric iron concentration. A single measurement took only a few minutes and was accurate to ± 5 ppm iron. A Phillips Norelco X-ray spectrograph was standardized beforehand using 5 ml aliquots of stock iron solutions. The response of the instrument in the concentration range of up to 1500 ppm iron was independent of the oxidation state of iron or the presence of phosphate in solution. A tungsten target tube and a lithium fluoride crystal were used for the determination with a flow proportional detector. The analysis line was the iron K-alpha with a wave length of 1.94 Å. The calibration curve, corrected for water background counts, followed the straight line equation

$$\text{ppm iron} = 0.112\,y$$

up to an iron concentration of 800 ppm, where y is the observed count per second. For the few determinations above 800 ppm, the iron concentration was read directly from the calibration curve.

A few initial ferric determinations were made iodometrically. The results agreed well with the X-ray values.

To make sure that only a negligible amount of the ferrous iron was oxidized to ferric during equilibration, a representative number of analyses were checked by oxidation-reduction titrations, using ceric sulfate and Ferroin indicator. No significant oxidation was detected.

TABLE I

Sequestration of Ferric Iron by Tetrasodium Pyrophosphate and Pentasodium Tripolyphosphate at 25C and pH 9

Total initial iron conc. in ppm	Total conc. of either polyphosphate, ppm	Parts of sodium polyphosphate to sequester one part iron[a]	
		Pyrophosphate	Tripolyphosphate
1000	5000	25.3	61.8
1000	2500	25.0	62.4
500	5000	22.3	61.8
300	5000	23.0	67.5
210	5000	23.8	65.0
100	5000	......	61.0
		Av. 23.9 ± 1.6	63.3 ± 4.2

[a] Weight ratio of total sodium polyphosphate to solubilized iron, in presence of ferric hydroxide precipitate.

Results and Discussion

An important problem in making sequestration measurements is to be sure that equilibrium is attained. The evidence for the equilibrium nature of our results is that they were independent of modes of addition of phosphate to iron to caustic, or to extended periods of equilibration (weeks). Also, we showed that at any specified pH value the ratio of concentrations of polyphosphate to soluble iron was independent of the initial total concentration of either iron or phosphate. Typical data, shown in Table I, strongly indicate the presence of a true complex and also show that the precision of a single value is ± 6.6% at the 95% confidence limits. Since most of the measurements were duplicates, our results are precise to better than ± 5%.

Ferric Sequestration. Ferric hydroxide is so insoluble that it precipitates at pH values as low as 1.5. Actually, very few precipitates containing iron are more insoluble than ferric hydroxide. Therefore, our ferric iron sequestration values represent competition between the insolubility of ferric hydroxide and the stability of ferric polyphosphate complexes.

Figure 1 shows that amounts of ferric iron sequestered in the pH range 4–11 at 25C by the various polyphosphates. During equilibration, the pH of the solution rose; the values shown in Figure 1 are those after equilibrium was achieved. It is clear that throughout this pH range the effectiveness to sequester ferric iron decreases with increase in polyphosphate chain length. No measurable dissolution of ferric hydroxide was observed in the presence of orthophosphate.

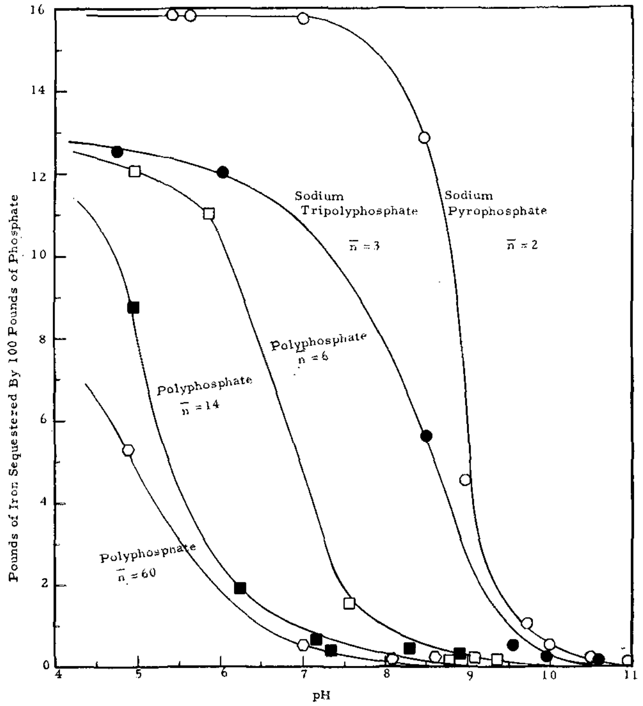

FIG. 1. Sequestration of Iron (III).

At low pH values, sequestration is fairly independent of pH. This can be explained on the basis that the ratio of the stability constant of the complexes to the solubility product of the ferric hydroxide is such that at low pH values most of the polyphosphate is in the form of the complex, and the amount of iron sequestered is simply determined by the molar ratio of iron to polyphosphate in the soluble complex. These ratios turn out to be 0.77 for $Fe^{3+}:P_2O_7$ and 0.87 for $Fe^{3+}:P_3O_{10}$. Since sodium ions complex some of the polyphosphates, it is reasonable to assume a 1:1 complex in both cases. Attempts to use spectrophotometry and Job's method of continuous variation to determine the formula of the complexes more accurately failed because of precipitate formation in alkaline solutions containing iron in excess of 1:1 mole ratio to polyphosphate.

Determination of the formula of the complex in acidic solutions were abandoned because it was found to change with pH in that region, coupled with complicated hydrolysis of the ferric ion by itself.

At pH values around 8, the insolubility of the ferric hydroxide becomes of the same order of magnitude as the stability of the ferric pyrophosphate and tripolyphosphate complexes. Results at pH values above this can be used to estimate the stability of the complexes, provided the concentration of free ferric iron in equilibrium with ferric hydroxide is known.

The total solubility of FeOOH, the accepted formula for the solid in equilibrium with Fe^{3+} and OH^- ions, at pH values greater than 5 has been explained (2) by the equilibrium:

$$FeOOH(s) + H_2O \rightleftharpoons Fe(OH)_3\text{, dissolved} \qquad (1)$$

The average value for the equilibrium constant in equation 1 over the pH range of 6–11 was found to be 2.9×10^{-7}. For more acidic solutions the interpretation of the solubility data proved to be difficult because of the simultaneous presence of a series of ferric hydrolysis products. Therefore, a total measurement of iron concentration cannot yield a meaningful solubility product, because it includes other iron species.

Biedermann and Schindler (1) used emf measurements of cell potentials that gave directly the concentrations of free Fe^{3+} and OH^- ions to calculate for

$$FeOOH(s) + H_2O \rightleftharpoons Fe^{3+} + 3\,OH \qquad (2)$$

a solubility product

$$(Fe^{3+})(OH^-)^3 = 10^{38.7\pm0.2} \qquad (3)$$

with the ionic product of water being taken as $10^{-14.22}$.

Using our data in the pH range 8–10 and equation (3) gave the following dissociation constants:

$$\frac{(Fe^{3+})(P_2O_7{}^{4-})}{(FeP_2O_7{}^{-})} = 10^{-23.2\pm1.5} \qquad (4)$$

$$\frac{Fe^{3+})(P_3O_{10}{}^{5-})}{(FeP_3O_{10}{}^{2-})} = 10^{-22.9\pm1.3} \qquad (5)$$

There is no way from the present data to decide upon including and excluding hydrogen ions in the complex. No attempts were made to calculate the constants involving the longer chain polyphosphates because of the difficulty involved in assigning a meaningful formulae for the complexes.

To assess the validity of our procedure for estimat-

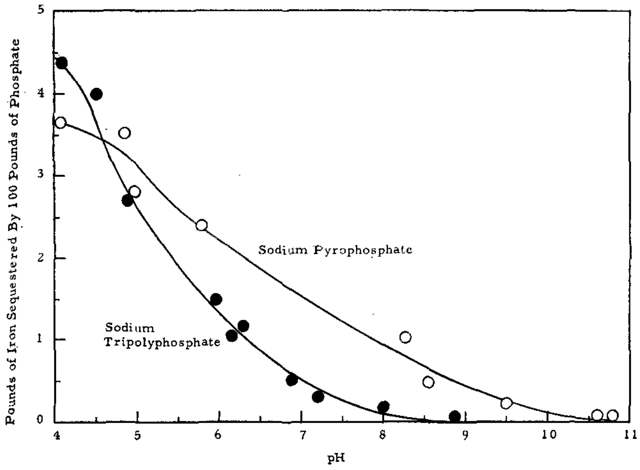

FIG. 2. Sequestration of Iron (II).

ing the stability constants, the stability constant for ferric ethylenediamine tetraacetate (EDTA) was determined and found to be:

$$\frac{(Fe^{3+})(EDTA^{4-})}{(FeEDTA^{-})} = 10^{-26.7\pm0.4} \qquad (6)$$

as compared with a literature (6,8) value of $10^{-25.1}$, obtained with more sophisticated methods. The agreement suggests that our assumptions are not grossly in error.

Ferrous Sequestration. The results for ferrous iron sequestration, shown in Figure 2, were obtained by allowing 1000 ppm of iron from $FeCl_2$ to come to equilibrium with 5000 ppm of sodium polyphosphates at various pH values.

Many authors listed in reference (2) found the solubility product of ferrous hydroxide to be in the range of 10^{-12} to 10^{-21}, depending on time of equilibration and degree of oxidation of ferrous ions. Our data cannot be rigorously interpreted with these values because in the pH region of 2–8, we found less dissolved iron in the presence of polyphosphates or EDTA than would be predicted from the solubility product of the ferrous hydroxide by itself. This must lead us to conclude that, though not detectable, some ferrous oxidation took place in our system leading to the formation of the more insoluble ferrosic hydroxides, $Fe(OH)_2 \cdot \times Fe(OH)_3$. However, rough estimates show ferrous polyphosphate complexes to have dissociation constants larger than 10^{-14}.

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Hydrogenation of Linolenate. VIII. Effects of Catalyst Concentration and of Temperature on Rate, Selectivity, and *Trans* Formation[1]

A. E. JOHNSTON, HELEN M. VEN HORST, J. C. COWAN, and H. J. DUTTON,
Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

The effects of catalyst concentration and of temperature on linolenate selectivity, *trans* formation, and rate of hydrogenation have been studied for a commercial electrolytic nickel catalyst. Results obtained with an equimixture of linoleate and linolenate, following the procedure previously described, are presented as isometric drawings, which cover the experimentally practicable temperature ranges from 70–230C and nickel concentration from 0.05–10%. Whereas the rate of hydrogenation depends upon both temperature and catalyst concentration, *trans* formation is essentially a function of temperature while selectivity is little influenced by either parameter.

Introduction

A PREVIOUS INVESTIGATION has shown that statistically significant differences do exist between commercially available catalysts in their linolenate selectivity and isomerization characteristics (8). The present phase of a continuing search for linolenate selectivity in reduction of linolenoyl groups and for low isomerizing tendencies concerns the influence of the parameters of temperature and percentage catalyst. It is part of a utilization research program aimed at the production of flavor-stable products high in linoleic acid by hydrogenation of soybean oil.

Experimental

A procedure to evaluate catalysts for selectivity has been previously described (5) and its applicability demonstrated in a survey of commercial catalysts (8). The specific details of manometric manipulation, gas-liquid chromatography, and infrared spectrometry were presented by Johnston et al. (8). Diene conjugation was determined on weighed samples in isooctane using a Carey Model 14 spectrophotometer. The catalyst selected for more intensive study from among those surveyed, because it demonstrated high-linolenate selectivity and moderate isomerization characteristics, is 25% nickel in cottonseed flakes prepared by electrolytic precipitation.

Results and Discussion

Experimental data from this investigation are presented in the form of three isometric drawings (Figs. 1, 2, and 3). In these three dimensional diagrams temperature and nickel concentration are plotted on

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[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.