could be detected. The freezing point of nitric acid was found to be −41.60 ± 0.05°, in good agreement with the results of Forsythe and Giauque[3] (−41.59°) and of Dunning and Nutt[4] (−41.62°).

Apparatus and Procedure.—The orthobaric density of nitric acid was measured with a pycnometer constructed by blowing a bulb of about 3-cm.^{3} capacity on the end of a 1-mm. bore capillary tube. A similar but much smaller bulb was blown on the other end of the capillary to serve as a reservoir for the expansion of the liquid at higher temperatures. The volumes of the bulbs and the volume/mm. of the capillary, from a reference line etched on the capillary, were very carefully determined by calibration with mercury.

The pycnometer was sealed directly to the high vacuum line of the nitric acid generator and was filled with pure nitric acid by condensing the vapors in the bulb, which was cooled with a mixture of carbon tetrachloride and Dry Ice. The pycnometer was then sealed off from the line at a previously prepared mark and was immersed in a water-bath whose temperature was held constant within ±0.02°. As soon as temperature equilibrium was attained, the height of the acid meniscus above the reference line was measured with a cathetometer reading to 0.05 mm. These observations were repeated at approximately 2–4° intervals up to about 33°. The total volume occupied by the liquid sample at each temperature was then calculated, a correction being applied for the complement of the acid meniscus.

The temperature was measured with a precision mercury thermometer and read with the aid of the cathetometer telescope to within 0.02°. The thermometer was compared over the entire range against a platinum resistance thermometer which had previously been tested at the U. S. Bureau of Standards.

At the termination of the observations, the pycnometer was dried and weighed with calibrated weights. The tip of the pycnometer was then broken off, the nitric acid completely removed and the empty pycnometer plus the tip dried and weighed. The weight of the nitric acid sample was obtained by difference. All weights were reduced to vacuum. The density was calculated from these data.

At the highest temperature, a very small amount of decomposition occurred as indicated by a very pale yellow color appearing in the otherwise water-white liquid.

Results.—The density was found to vary linearly with the temperature over the range investigated, namely, 1.00–32.33°, and could be expressed by the equation

$$d(\text{g./cm.}^3) = 1.5492 - 0.00182t(^\circ\text{C.})$$

which was fitted by the method of least squares. The accuracy of the measurements is within ±0.0001 g./cm.^{3}. The experimental results are given in Table I.

TABLE I

THE ORTHOBARIC DENSITIES OF ANHYDROUS NITRIC ACID

Temp., °C. ± 0.05°	Density, g./cm.^{3} ± 0.0001	Temp., °C. ± 0.05°	Density, g./cm.^{3} ± 0.0001
1.00	1.5475	13.28	1.5249
1.74	1.5460	14.07	1.5234
2.61	1.5443	19.60	1.5136
4.20	1.5415	21.35	1.5105
9.52	1.5319	23.80	1.5059
10.50	1.5302	27.78	1.4989
10.90	1.5294	29.88	1.4948
12.70	1.5260	32.33	1.4905

A comparison of the values of the density as given by the equation with values reported in the literature is shown in Table II.

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[3] W. R. Forsythe and W. F. Giauque, THIS JOURNAL, **64**, 52 (1942).

[4] W. J. Dunning and C. W. Nutt, *Trans. Faraday Soc.*, **47**, 22 (1951).

TABLE II

COMPARISON OF MEASURED DENSITIES OF PURE NITRIC ACID WITH LITERATURE VALUES

Temp., °C.	Literature	Density, g./cm.^{3} from eq. 1	Exptl. − lit.
0	1.54786[5]	1.5492	0.0013
0	1.5472[6]	1.5492	.0020
5	1.5402[7]	1.5401	− .0001
10	1.5310[7]	1.5310	.0000
12.5	1.5245[6]	1.5264	.0019
15	1.52150[5]	1.5219	.0004
15	1.5217[7]	1.5219	.0002
20	1.5129[7]	1.5128	− .0001
24.9	1.5033[8]	1.5039	.0006
25	1.5018[6]	1.5037	.0019
25	1.5040[7]	1.5037	− .0003
30	1.4952[7]	1.4946	− .0006

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[5] K. Mischtschenko, *Z. Prikladnoj Chim.*, **2**, 525 (1929).

[6] A. Klemenc and J. Rupp, *Z. anorg. Chem.*, **194**, 55 (1930).

[7] Reference 2.

[8] E. Briner, B. Susz and P. Favarger, *Helv. Chim. Acta*, **18**, 376 (1935).

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Spectrophotometric Evidence of Polymerization in Peroxytitanic Acid Solutions

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RECEIVED MAY 21, 1954

It has been well established through the work of Schaeppi and Treadwell[2] and others[3] that, in acid solution, titanic acid and hydrogen peroxide react in the one to one molar proportion to produce highly colored peroxytitanic acid. The color produced by this reaction has been the basis for many quantitative methods for the determination of titanium or peroxide in solution. It has been recognized by several workers that the light absorption of peroxytitanic acid solutions obeys Beer's law only at rather great dilutions, but a search of the literature has failed to reveal either a description of the nature of the deviations from the ideal behavior, or a satisfactory explanation of the cause for these effects.

In a general study of the flameproofing potentialities of titanium compounds we have investigated the absorption characteristics of peroxytitanic acid solutions in the concentration ranges where deviation from Beer's law is very pronounced. Some of our results are reported in this communication, and a possible explanation of the behavior of concentrated peroxytitanic acid solutions is advanced.

Experimental

Titanium sulfate solutions were prepared by adding a known weight of redistilled tetraisopropyl titanate to ice-cold 5 *N* sulfuric acid, shaking the chilled mixture until solution was complete, and diluting to the desired concentration. It was established in separate experiments that the analytically pure tetraisopropyl titanate could be handled with

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[2] Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

[3] Several references are given in "Gmelin's Handbuch der anorganischen Chemie," 8th Ed., System No. 41, pp. 269–270.

sufficient precision to allow it to be employed as a primary standard in calculating titanium concentrations.

Absorption spectra measurements were made in a Cary recording spectrophotometer employing quartz cells having optical paths of such lengths that the peak absorbancies ranged between 0.7 and 2.45. The composition of the reference solution differed from that of the colored solutions only in the absence of titanium.

Discussion of Results

The molar absorptivity (ϵ) for peroxytitanic acid at various concentrations in molar sulfuric acid solution are shown in Fig. 1. The uppermost curve represents the concentration range where Beer's law is obeyed. Under the conditions of these experiments this region extends up to about one millimole of peroxytitanic acid per liter. The shape of this curve, the location of the maximum at 410 mμ, and the magnitude of ϵ at the maximum are almost identical with the corresponding values calculated from the data of Weissler[4] for dilute solutions of peroxytitanic acid in perchloric acid. These facts make it appear unlikely that peroxytitanic acid forms a complex with either the sulfate or the perchlorate anion.

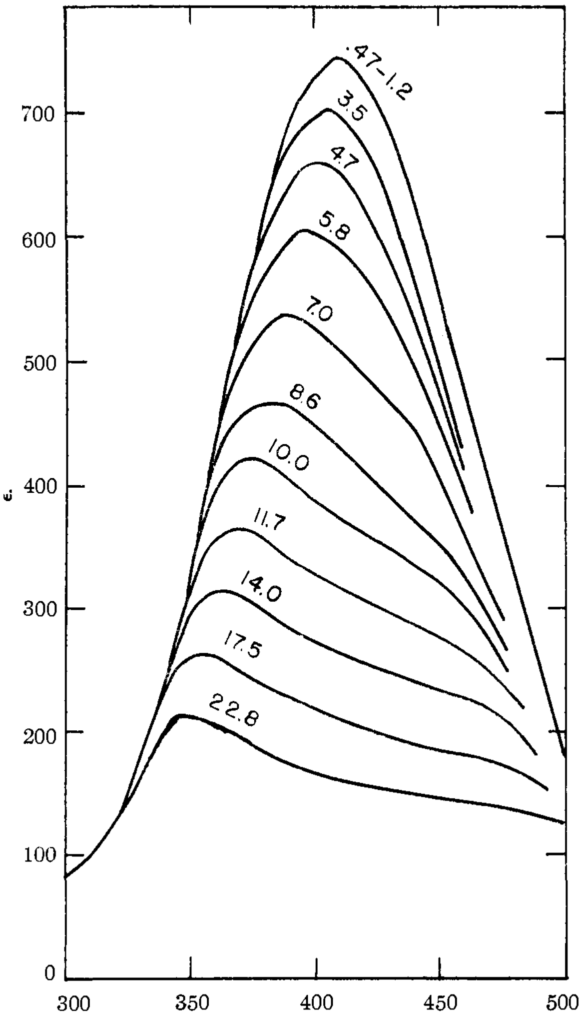

Fig. 1.—Molar absorptivities for peroxytitanic acid in solutions containing one mole of sulfuric acid and 0.15 mole of hydrogen peroxide per liter. The concentrations of titanium are indicated in the figure in moles per liter $\times 10^3$.

With increasing concentrations of peroxytitanic acid the curves of Fig. 1 show a gradual shift to shorter wave lengths, and a pronounced decrease in the magnitude of the molar absorptivity throughout the region between 350 and 475 mμ. A family of curves such as is shown in the figure could not result from a small number of absorbing species. Rather, it would require a relatively large number of closely related absorbing species to produce this series of curves.

Formation constants for the formation of a dimer were calculated employing molar absorptivities at 410 mμ, assuming the highest curve of Fig. 1 to represent the monomer and the lowest curve, the dimer. These calculated "constants" ranged from 1.2×10^{-3} to 4×10^3, hence the family of curves cannot be interpreted as representing a simple dimerization. Similar calculations were made, but with the assumption that the middle curve represented the absorptivity of the dimer. In this case the values ranged from 2.6 to 840. Consideration of the trends in the calculated dimer formation "constants" indicates that the true absorptivity of the dimer lies well above that of the middle curve. If this is the case it is probable that more than three absorbing species occur in the concentration ranges which were examined.

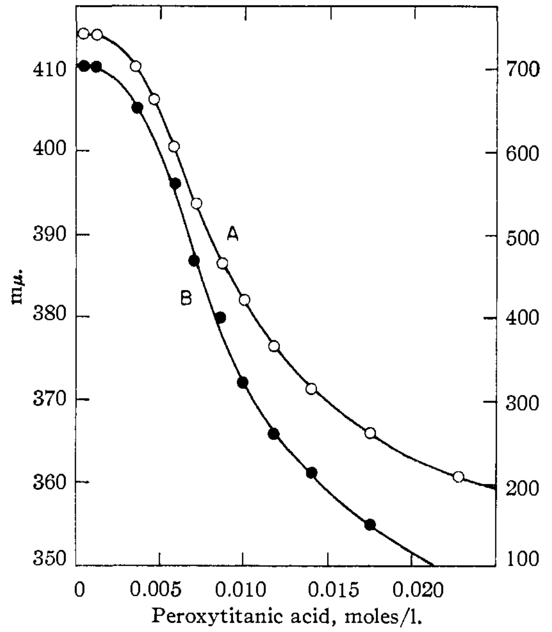

Fig. 2.—Curve A, the relationship between the magnitude of the maximum molar absorptivity (ϵ), and the concentration of peroxytitanic acid; curve B, the relationship between the position in mμ of the peak and the concentration of peroxytitanic acid.

Figure 2 shows two features of the family of curves of Fig. 1 plotted against the concentration of peroxytitanic acid. Curve A shows changes in the magnitude of ϵ at the peaks; curve B, changes in position of the peaks. These curves emphasize the gradual nature of the transitions which occur with increasing peroxytitanic acid concentrations.

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(4) A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 695 (1948).

We regard these results as indicative of the formation of a series of closely related polymers in moderately concentrated peroxytitanic acid solutions. In the dilute concentration range where Beer's law is obeyed the solutions contain only the peroxytitanic acid monomer, but at higher concentrations equilibrium mixtures of polymeric species occur, accounting for the gradual transition in the absorption characteristics of the solutions. This view is supported by the observation that increasing peroxytitanic acid concentrations do not produce increased molar absorptivities in any part of the visible or near ultraviolet spectrum, but rather a general decrease in absorption, which is indicative of a stabilization of the electronic system of titanium as polymerization progresses.

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Preparation and Properties of Anhydrous Trisodium and Tripotassium Monothiophosphates

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As part of a study of monothiophosphate salts as primary standard reducing reagents for iodometry, pure anhydrous trisodium monothiophosphate and tripotassium monothiophosphate were prepared and characterized. When anhydrous, the sodium salt is very stable at room temperature and may be heated at 100° without decomposition. It does not absorb moisture from the air at relative humidities below 31%. Hydrated trisodium monothiophosphate, $Na_3PO_3S \cdot 12H_2O$, the only one reported previously in the literature, decomposes slowly at room temperature as indicated by the odor of hydrogen sulfide above the solid salt, and decomposes rapidly at 60°.

The potassium salt prepared by this method was contaminated by potassium chloride, but probably could be obtained pure after a sufficient number of recrystallizations. Tripotassium monothiophosphate, which apparently has no water of hydration, was previously reported to be obtainable only in solution.[1]

Experimental

The reaction of sodium or potassium hydroxide solution with thiophosphoryl chloride[2]

$$PSCl_3 + 6NaOH = Na_3PO_3S + 3NaCl + 3H_2O$$

is an unequivocal method for obtaining the respective monothiophosphate salt without the di-, tri-, or tetrathiophosphate being formed at the same time. The only nonvolatile by-product is the alkali metal chloride.

Preparation of Thiophosphoryl Chloride.—The method of Knotz[3] was found to be the most convenient method for preparation on a laboratory scale. Phosphorus trichloride (54.6 ml.) and powdered sulfur (20.1 g.), with anhydrous aluminum chloride (approximately 2 g.) added as catalyst, reacted under reflux. The reaction is often vigorous, although slight heating may be necessary to get it started. The reaction products are distilled and the fraction boiling between 120 and 125° is collected.

Preparation of Anhydrous Trisodium Monothiophosphate.—Sodium hydroxide (40.0 g.) in 300 ml. of aqueous solution is heated with thiophosphoryl chloride (17.5 ml.) under reflux at 110–115° for 15 minutes or more, until the thiophosphoryl chloride layer has disappeared. The solid trisodium monothiophosphate and sodium chloride salts separate out on cooling in an ice-bath. These are filtered off and dissolved in a minimum quantity of warm (40–45°) water. For each 100 ml. of salt solution, approximately 185 ml. of anhydrous methanol is added to precipitate the trisodium monothiophosphate hydrated salt. This recrystallization procedure is repeated, and the hydrated salt dehydrated by suspending with constant stirring for one hour in 200 ml. of anhydrous methanol. The white anhydrous trisodium monothiophosphate crystals are filtered with suction at room temperature, heated at 100° for one hour, and stored in a tightly stoppered bottle.

The anhydrous trisodium salt decomposes without melting at 120–125° to release a volatile compound which discolors lead acetate paper. Solubilities in grams per liter of saturated solution at various temperatures are: 4°, 21.2; 18°, 79.2; 28°, 132.7; 38°, 241.5. Solutions of the sodium salt decompose slowly, but are apparently stable when stabilized with added sodium carbonate.

Anal. Calcd. for Na_3PO_3S: S, 17.83; P, 17.27. Found: S, 17.90, 17.78, 17.90, 17.68, 18.06; P, 17.09, 17.38, 17.25.

Sulfur was determined by oxidation to the sulfate and weighed as barium sulfate. Phosphorus was oxidized to the phosphate and weighed as magnesium ammonium phosphate. Titration with standard iodine solution in the *p*H range 0.5–0.8, using a potentiometric end-point with polarized platinum electrodes, gave consistent results between 99.9 and 100.0% of calculated purity, assuming the reaction[4]

$$2PO_3S^{=} + 2H^{+} + I_2^{-} \longrightarrow (HO_3PSSPO_3H)^{=} + 2I^{-}$$

Preparation of Tripotassium Monothiophosphate.—The preparation of the tripotassium monothiophosphate is similar to that of the sodium salt, except that 56.1 g. of potassium hydroxide in concentrated aqueous solution is treated with 17.5 ml. of thiophosphoryl chloride. Purification is attained slowly by repeated recrystallizations with methanol, but it is very difficult to remove potassium chloride completely, probably because of the slight solubility of potassium chloride in methanol–water solution. The gravimetric determination of sulfur as barium sulfate, and phosphorus as magnesium ammonium phosphate, agreed well with the degree of purity indicated by the iodimetric method using the potentiometric endpoint described above.

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[1] C. Kubierschky, in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., New York, N. Y., 1931, p. 1069.

[2] C. A. Wurtz, ref. 1, pp. 1068–1069.

[3] F. Knotz, *Osterr. Chem. Z.*, **50**, 128 (1949).

[4] E. Thilo and E. Schöne, *Z. anorg. Chem.*, **259**, 225 (1949).