the concentration was checked by an iodometric titration, and a good agreement was obtained with concentrations calculated from the weight of the sample. Every precaution was taken not to expose the solution to atmospheric moisture more than it was absolutely necessary. Two concentration ranges were used, depending on the region investigated. The solutions were approximately 10^{-3} M for measurements in the 380–260 mμ range, and 10^{-5} M in the 260–210 mμ range.

Absorption measurements were made on a Beckman model DU spectrophotometer and the final runs were on a Cary recording spectrophotometer model 11. Matched silica cells of 1-cm. path length were used. The experiments were carried out at room temperature, which was approximately 25°.

Preliminary measurements showed that the absorption spectrum of the tetrachloroiodide complex did change with time. Fresh solutions of this complex gave two maxima, one at 214 mμ with a molar absorbancy index of 42000,[5] and a second at 340 mμ with a molar absorbancy index of 1280. In about 30 minutes it was noticed that the absorbancy of the first peak increased and the maximum was shifted toward longer wave lengths, while the second maximum remained at the same wave length, but decreased in absorbancy.

A time study of this change of absorption is illustrated in Fig. 1. After 24 hours the maxima were at 227 and 338 mμ with the molar absorbancy indices of 55000 and 410, respectively. No further change of the absorption spectrum with time was observed.

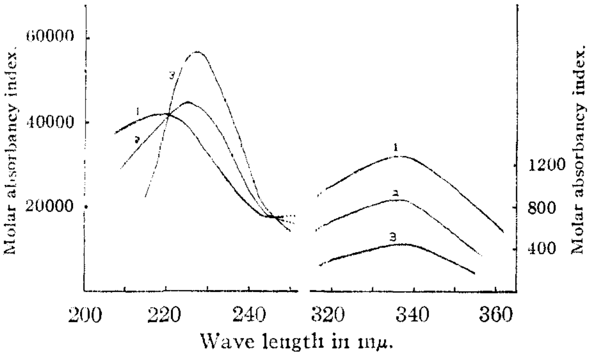

Fig. 1.—Absorption spectrum of trimethylsulfonium tetrachloroiodide in acetonitrile: curve 1, fresh solution; curve 2, after 2.5 hours; curve 3, after 24 hours.

The absorption curve of the dichloroiodide complex in acetonitrile is given in Fig. 2. The solution appeared to be stable and did not change the absorption spectrum with time. It is seen that this curve essentially coincides with the 24-hour old curve of the tetrachloroiodide complex. Presence of two isobestic points (Fig. 1) at 219 and 245 mμ shows that only two absorbing species were present in solution, and therefore the conclusion is warranted that the tetrachloroiodide ion dissociated in acetonitrile to the dichloroiodide and chlorine.

Undoubtedly, a fast equilibrium $(CH_3)_3SICl_4 \rightleftarrows (CH_3)_3SICl_2 + Cl_2$ is established, and curve 1, Fig. 1, illustrates the equilibrium conditions.

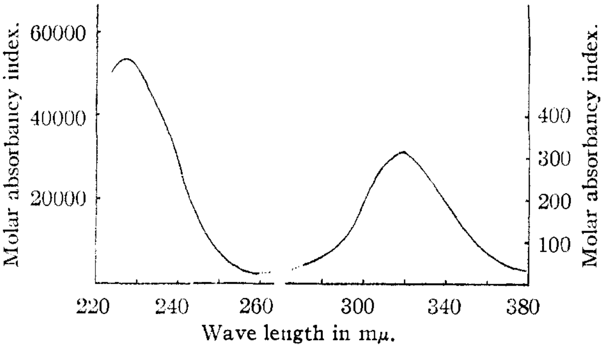

Fig. 2.—Absorption spectrum of trimethylsulfonium dichloroiodide in acetonitrile.

The slow reaction observed is very probably due to the shift in equilibrium because of removal of chlorine by the chlorination of the solvent.

Since the tetrachloroiodide ion can be considered as a complex of iodine trichloride with Cl^-, it seems interesting to note that apparently this complex formation stabilizes iodine trichloride to some extent. It has been fairly well established that iodine trichloride molecule is stable only in the solid state[6] and dissociated in solution, immediately and completely, to iodine chloride and chlorine. If this was the case with the tetrachloroiodide complex, the initial absorption curve should be a composite curve of ICl_2^- and Cl_2. That this is not the case is easily seen from the fact that the absorbancy increases with time at 227 mμ. Attempts were made to obtain absorption curves of iodine trichloride and of chlorine in acetonitrile, but the results were unsatisfactory, because, in order to obtain sufficient amount of absorption, comparatively concentrated solutions ($\geqslant 10^{-2}$ M) had to be prepared and under these conditions the chlorination of the solvent was quite rapid.

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(5) Nomenclature used in this paper follows the recommendations of the National Bureau of Standards, Letter Circular, LC-857 (1947).

(6) A. E. Gillam and R. A. Morton, *Proc. Roy. Soc.* (*London*), **A124**, 604 (1929).

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A Polarographic Study of Thallium Pyrophosphate Complexes

BY PASCHOAL SENISE[1] AND PAUL DELAHAY

RECEIVED MARCH 6, 1952

Polarographic studies of pyrophosphate complexes of various metals have been reported by Sartori,[2] Rogers and Reynolds,[3] Laitinen and Onstott[4] and Reynolds and Rogers.[5] In these investigations, no mention is made of the formation of thallium pyrophosphate complexes; and it is the purpose of the present paper to report a quantitative study of such compounds.

Experimental

Preliminary measurements were made with a Sargent model XI polarograph. Final waves were determined point

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(1) On leave from Faculdade de Filosofia, Ciencias e Letras da Universidade de Sao Paulo, Sao Paulo, Brazil.

(2) G. Sartori, *Gazz. chim. ital.*, **64**, 3 (1934).

(3) L. B. Rogers and C. A. Reynolds, THIS JOURNAL, **71**, 2081 (1949).

(4) H. A. Laitinen and E. I. Onstott, *ibid.*, **72**, 4729 (1950).

(5) C. A. Reynolds and L. B. Rogers, *Anal. Chem.*, **21**, 176 (1949).

by point by measuring the current and the voltage with a Sargent polarograph model III and a Leeds and Northrup student potentiometer, respectively. An H-cell[6] was used throughout the work. The rate of flow of mercury and the drop time, measured at −0.7 volt (*vs.* S.C.E.), were as follows: m = 2.31 mg. sec.$^{-1}$ and t = 3.10 sec. C.P. reagents were used without further purification. Except when otherwise indicated, the solutions were 0.2 molar with respect to potassium hydroxide and the ionic strength was adjusted at a value of 2.0 by addition of potassium nitrate. Gelatin was used as a maximum suppressor at a concentration of 0.01%. All measurements were made at 35 ± 0.1°.

In the study of the influence of *p*H, the pyrophosphate solutions were buffered with acetic acid for *p*H's below 6 and with boric acid for *p*H's between 6 and 8. In other experiments in which the *p*H was comprised between 7.5 and 8.5, the Kolthoff[7] buffer (monopotassium phosphate and borax) was used. For *p*H's between 8.5 and 11 the Britton and Welford[7] buffer of monopotassium phosphate and sodium hydroxide were employed. For higher *p*H's only potassium hydroxide was used.

Description and Discussion of Results

Influence of *p*H.—Experiments carried out in solutions buffered at different *p*H's but at the same ionic strength (μ 1.5) and constant sodium pyrophosphate concentration (0.1 *M*), showed that the diffusion current decreases as the *p*H is increased up to 9.5. With more alkaline solutions, the current is independent of *p*H. This variation of the diffusion current is probably caused by the progressive ionization of pyrophosphoric acid and pyrophosphate ions and the resulting changes in the nature of the thallium complexes. Extreme values of the diffusion current for a millimolar thallium solution were as follows: 5.66 microamp. at *p*H 4.5, and 3.64 microamp. at, and above, *p*H 9.5.

Influence of Concentration of Pyrophosphate.—The half-wave potentials and diffusion currents for various concentrations of pyrophosphate at a constant ionic strength of 2 (except for the highest concentration of pyrophosphate) are given in Table I.

TABLE I

DATA FOR 0.2 MILLIMOLAR THALLIUM SOLUTION IN 0.2 *M* POTASSIUM HYDROXIDE

$Na_4P_2O_7$, moles per l.	$E_{1/2}$,[a] volt *vs.* S.C.E.	i_d, microamp.
0.000	−0.4887	1.19
.012	− .4959	1.04
.033	− .5075	0.90
.057	− .5163	.82
.093	− .5257	.77
.116	− .5310	.74
.141	− .5387	.73
.166	− .5466	.70
.187	− .5520	.69

[a] $E_{1/2}$ reproducible within 0.001 volt.

By plotting $E_{1/2}$ against the logarithm of the concentration of pyrophosphate a curve is obtained. This indicates the formation of at least two complexes, and consequently the classical polarographic method of determining unstability constants[8] is not applicable. The formation constants for the various complexes, however, can be calculated by the method recently reported by DeFord and Hume.[9,10] In this treatment one calculates the functions

$$F_0 = \text{antilog}\left\{0.435\,\frac{nF}{RT}\,[(E_{1/2})_S - (E_{1/2})_C] + \log\frac{I_S}{I_C}\right\} \quad (1)$$

$$F_1 = [F_0 - K_0/f_S]C_Xf_X \quad (2)$$

$$F_j = [F_{j-1} - K_{j-1}/f_{MX}]/C_Xf_X \quad (3)$$

where $(E_{1/2})_S$ and $(E_{1/2})_C$, I_S and I_C are the half-wave potentials and the diffusion currents of the waves for the simple ion and the complexes, respectively; K_0 is equal to unity; K_j is the formation constant of the complex of jth order; and C_x is the concentration of the complex forming substance.

In the present case the complexes $\mathrm{Tl(P_2O_7)}_j^{(4j-1)-}$ which could possibly exist correspond to the following values of j: $^1/_4$, $^1/_3$, $^1/_2$, 1, 2, ... In order to determine whether the complex corresponding to $j = {}^1/_4$ is formed one should consider the function

$$F_{1/4} = [F_0 - K_0/f_S]/C_X^{1/4}f_X \quad (4)$$

whose limit is $K_{1/4}$ when C_X approaches zero. This function $F_{1/4}$ was calculated, and it was concluded by extrapolating its value to $C_X = 0$ that $K_{1/4} = 0$, *i.e.*, that the undissociated pyrophosphate $\mathrm{Tl(P_2O_7)}_{1/4}$ virtually does not exist in solution. Likewise, by plotting $F_{1/3}$ *vs.* $C_X^{1/3}$, and $F_{1/2}$ *vs.* $C_X^{1/2}$, it was concluded that the complexes $\mathrm{Tl(P_2O_7)}_{1/3}^{1/3}$ and $\mathrm{Tl(P_2O_7)}_{1/2}$ are not formed under the present conditions. On the other hand, by plotting F_1 *vs.* C_X (Fig. 1), the value $K_1 = 49 \pm 8$ was obtained for the formation constant corresponding to the complex $\mathrm{Tl(P_2O_7)^{-3}}$. The extreme values of F_1 shown in Fig. 1 were calculated by assuming that the precision for the quantity $[(E_{1/2})_s - (E_{1/2})_c]$ of equation (1) was ±0.002 volt and that the currents I_s and I_c were measured within ±1%. Likewise, the function F_2 (Fig. 1) was calculated on the basis of the extreme values of F_1. By extrapolating F_2 to zero concentration of pyrophosphate one obtains $K_2 = 75 \pm 75$. The plot of F_2 ***versus*** the concentration of pyrophosphate still exhibits a marked curvature, and consequently at least the complexes of 3rd and 4th order should be considered.[9] The calculation of K_3 and K_4, however, is rather meaningless because the errors on F_3 and F_4 are too large.

It should be added that, in the above calculations, all the activity coefficients were assumed to be equal to unity, as was done by Hume, *et al.*, in the study of cadmium thiocyanate complexes. Therefore, the above formation constants should be regarded as formal constants for an ionic strength of 2. In the present case, the charges of the complex ions are large, and consequently the activity coefficients are undoubtedly much smaller than one. As a result, the discrepancies between the above formal constants and the corresponding thermodynamic data are probably quite pronounced. Furthermore, liquid junction potentials were assumed to be constant regardless of the concentration of pyrophosphate ion. It is true that the ionic strength was constant in our experiments, but nevertheless the composition of the medium

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[6] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 504 (1939).

[7] H. T. S. Britton, "Hydrogen Ions," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 307.

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, Chap. X.

[9] D. D. DeFord and D. N. Hume, THIS JOURNAL, **73**, 5321 (1951).

[10] D. N. Hume, D. D. DeFord and G. C. B. Cave, *ibid.*, **73**, 5323 (1951).

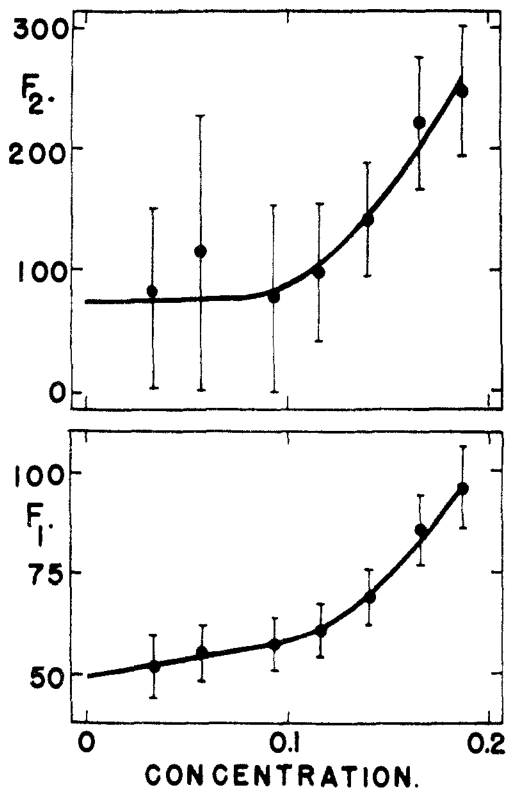

Fig. 1.—Variations of functions F_1 and F_2 with the concentration of pyrophosphate (in moles per l.). See data in Table I.

was changed, and this caused a variation of the liquid junction potential. However, the resulting error was probably small (less than 0.001 volt) since a saturated solution of potassium chloride was used in the junction.

Summarizing, the existence of various pyrophosphate complexes of Tl(+1) was demonstrated. The species $Tl(P_2O_7)^{-3}$ is predominant in the neighborhood of *p*H 13, but complexes of a higher order also exist; their formation constants, however, can only be determined in a very approximate manner by the polarographic method.

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The Systems Ammonia-Sulfamide and Sulfuric Acid-Sulfamide

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Several studies[1,2] of the behavior of acid amides toward basic and acidic solvents have been carried out in recent years. As part of this program, we were interested in investigating the binary systems ammonia-sulfamide and sulfuric acid-sulfamide.

Experimental

Materials.—Anhydrous sulfuric acid was prepared by adding the calculated amount of fuming sulfuric acid to chemically pure concentrated sulfuric acid which had been checked to assure the absence of nitric acid. The purity of the anhydrous sulfuric acid thus obtained was checked by determining its freezing point. The freezing point of our product was 10.3° (lit. 10.31°). The freezing point was rechecked before each sample of the acid was taken.

Anhydrous ammonia of the synthetic grade with a stated purity of 99.9% was used. Its purity was also checked by its freezing point; found −77.8° (lit. −77.74°).

Sulfamide was prepared by the reaction of sulfuryl chloride with an excess of anhydrous ammonia in the vapor state. A stream of dry nitrogen was passed through a dilute solution of sulfuryl chloride in petroleum ether. The gas stream (containing entrained sulfuryl chloride) was then passed into a reaction flask into which a large excess of gaseous ammonia was being passed. The solid products of the reaction were dissolved in water which was made slightly acidic with hydrochloric acid. After the solution had stood for at least 48 hours, the solution was evaporated to a very small volume under an infrared lamp in a current of dry air. The height of the lamp was adjusted so as to maintain a temperature between 50 and 60° in the evaporating solution. The small volume of remaining solution was then placed in a vacuum desiccator over calcium chloride to crystallize. The dried crystals were extracted with ethyl acetate, the ethyl acetate evaporated, and the crystals obtained dried in a vacuum desiccator. The sulfamide was further purified by another recrystallization from ethyl acetate. The product melted sharply at 91.5° (uncor.) (lit. 91.5-93.0°). Yields approximating 30 to 35% based upon the sulfuryl chloride used were obtained.

The System Sulfuric Acid-Sulfamide.—It was observed immediately that when samples of anhydrous sulfuric acid and sulfamide are mixed a clear solution is obtained, but that, if the solution stands for from 15 to 30 minutes at room temperature, a white solid begins to appear. This crystalline white solid was removed and shown by analysis and determination of the melting point to be virtually pure sulfamic acid. The reaction was also carried out in pure nitromethane and it was shown that, in the presence of excess sulfuric acid, the solvolytic reaction represented by the equation

$$SO_2(NH_2)_2 + SO_2(OH)_2 \longrightarrow 2SO_2(NH_2)(OH)$$

takes place quantitatively to yield sulfamic acid, which may be filtered off and isolated. Typical analytical results are listed in Table I.

TABLE I

	Experimental	Calcd. for $SO_2(NH_2)(OH)$
Sulfur(VI), %	31.8, 32.2, 32.1	33.0
Equiv. wt.	96.3, 96.5, 96.4	97.1

Melting point 203° (uncorrected) (lit. 205).

The System Ammonia-Sulfamide.—This binary system was investigated by the cryoscopic method and a phase diagram for the system constructed. The freezing point cell used is shown in Fig. 1. The thoroughly cleansed and dried cell was flushed out with dry nitrogen and the two side arms stoppered. A weighed sample of sulfamide was introduced through side arm B, the side arm sealed, and the whole cell and contents weighed. The desired amount of ammonia was introduced into the cell through side arm A and condensed by a Dry Ice-$CHCl_3$-CCl_4 cooling mixture. The rate of condensation of ammonia was followed by means of a flowmeter in the line. After the desired quantity of ammonia had been condensed, the side arm A was sealed, and the cell allowed to come to room temperature and weighed. The freezing points of the mixtures thus obtained were determined by means of cooling curves recorded, as described in previous publications from this Laboratory, on a Micromax self-recording potentiometer connected to a copper-constantan thermocouple placed in the well (C) of the cell. Constant stirring was provided by an intermittently actuated solenoid around the neck of the cell and a glass stirrer (E) which contained an iron slug (D) in its upper end. The thermocouple was covered with 2,3-dimethylpentane to minimize convection effects in the thermocouple well. The precautions observed and the techniques used in taking the freezing points were essentially the same as described in previous publications from this Laboratory.[3] The freezing

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(1) H. H. Sisler, A. W. Davidson, R. Stoenner and L. Lyon, THIS JOURNAL, **66**, 1888 (1944).

(2) H. H. Sisler, C. A. VanderWerf and S. Stephanou, *ibid.*, **68**, 2538 (1946).

(3) B. Rubin, H. H. Sisler and H. Schechter, *ibid.*, **74**, 877 (1952).