PREPARATION AND CHARACTERIZATION OF SALTS OF TRIAMINOGUANIDINE

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PREPARATION AND CHARACTERIZATION OF SALTS OF TRIAMINOGUANIDINE

By

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TABLE OF CONTENTS

INTRODUCTION

I - INTRODUCTION

Current interest in the uses of hydrazine and various other higher nitrogen content compounds has prompted a more detailed study of triaminoguanidine and its salts.

Salts of triaminoguanidine have been prepared by the hydrazinolysis of carbon tetrachloride [1], aminoguanidine [2], isothiourea ethers [3], dichloroformoxime [4], and more recently of guanyl azide [5]. Of these methods, the first has been attempted but never successfully repeated; and the synthesis from dichloroformoxime is somewhat complicated. The remaining syntheses are more or less similar.

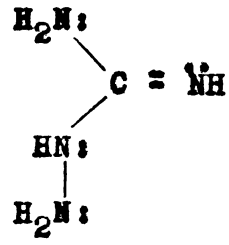
The purpose of the research reported herein was to prepare several salts of triaminoguanidine and to study their characteristics.

A study of salts of aminoguanidine[6] has shown that both mono- and di-acid salts can be prepared, including the bromide, chloride and nitrate. Two different sulfates can also be prepared, a "normal" sulfate and a "bisulfate".

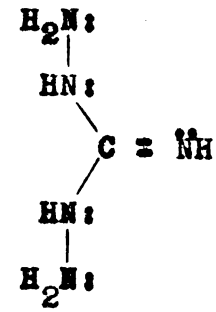
Recent studies of diaminoguanidine[7] indicate that di-acid salts can easily be prepared. As with aminoguanidine, two different sulfates were prepared, $(DAGH^{+})_2SO_4^{=}$ and $(DAGH_2^{++})\ SO_4^{=}$.

An explanation can be given for the above observations by noting the possible structures of these guanidine derivatives and their unshared pairs of electrons.

Aminoguanidine



Diaminoguanidine

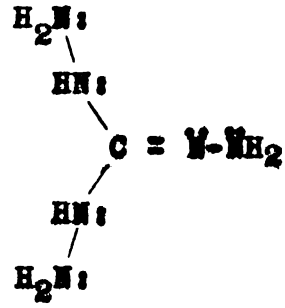


In each of the above compounds the imino nitrogen would be surrounded by the greatest electron density because of the carbon-nitrogen double bond; therefore, the first proton to become attached to the molecule would probably be held by the imino nitrogen. After this first proton is accepted the resulting ion would still be unsymmetrical with regard to the groups attached to the carbon atom. This condition would favor the addition of another proton giving rise to the di-acid salts and explaining the existence of two different sulfates, $(DAGH^{+})_2SO_4^{=}$ and $(DAGH_2^{++})\ SO_4^{=}$.

By the same reasoning, the behavior of triaminoguanidine can be explained. A possible electronic

configuration with the unshared pairs of electrons is shown.

Triaminoguanidine

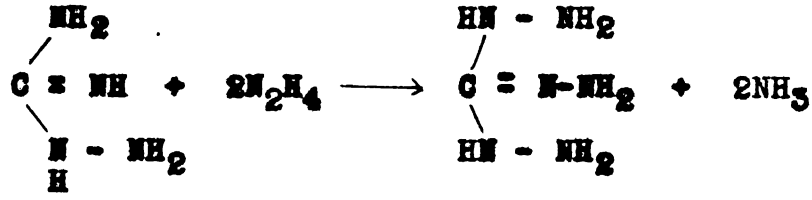


As in aminoguanidine and diaminoguanidine the first proton would probably become attached to the nitrogen atom with the greatest electron density. In this case it would also be the nitrogen doubly bonded to the carbon atom. Once a proton was accepted, there would be three equivalent groups attached to the carbon atom. The electronic charge will then be distributed symmetrically over the molecule and the mono-protonated compound would be very stable. This belief is supported by failure to prepare di-acid salts of triaminoguanidine.

PREPARATION OF SALTS

II - PREPARATION OF SALTS

The nitrate, chloride, and bromide salts of triaminoguanidine were prepared according to the method of Pellizzari and Gaiter.[2]



A - TRIAMINOGUANIDONIUM NITRATE

Twenty-seven grams, (0.2 mole), of aminoguanidonium bicarbonate was suspended in 250 ml. of water. To this was added slowly 12.5 ml. (0.2 mole), of concentrated nitric acid, then 24 ml. of $N_2H_4 \cdot H_2O$ (0.4 mole) as an 85% aqueous solution.

The reaction mixture was heated to boiling for three hours, water being added to maintain a constant volume; it was then evaporated to about one-half its volume on the steam bath. Upon cooling, the solution took on a pink color and long needle-like crystals formed. The material was filtered and washed with ethanol and ether. After concentrating the filtrate and cooling again several times, more of the product could be obtained. The collected fractions were then recrystallized from water, washed with ethanol and

dried in vacuo over porous barium oxide. The material melted at 215° C., with decomposition, in agreement with that of 216° C. reported by Pellizzari.

The salt was analyzed for hydrazine content according to the empirical method developed by Keim, Henry and Smith.[8] When using iodate solution as an oxidant for the analysis of hydrazine these workers found that it was necessary to apply a correction factor of 3/2.5 in order to explain their experimental data. This factor was used in all hydrazine analyses herein reported except as noted. Calculated for triaminoguanidonium nitrate:

57.36% N_2H_4

Found: 56.85% N_2H_4

B - TRIAMINOGUANIDONIUM BROMIDE

The bromide salt of triaminoguanidine was prepared the same way as the nitrate except that hydrobromic acid was used in place of the nitric acid. Upon cooling the reaction solution the pink color was again developed together with similar white, long needle-like crystals. The product was filtered, washed with ethanol and dried over barium oxide. The observed melting point was 223° C., with decomposition,

as compared to 232° C. reported by Pellizzari. This melting point, however, could not be raised appreciably by recrystallizations. Calculated for triaminoguanidonium bromide:

	52.0%	N_2H_4
	43.19%	Br^-
Found:	52.2%	N_2H_4
	43.29%	Br^-

C - TRIAMINOGUANIDONIUM CHLORIDE

The chloride salt of triaminoguanidine was prepared as described above for the nitrate and bromide.

The product again was a mass of white, needle-like crystals. After drying, the salt melted with decomposition at 223° C., compared to 231° C. as reported by Pellizzari. Recrystallization did not raise the melting point. Calculated for triaminoguanidonium chloride:

	68.6%	N_2H_4
	25.23%	Cl^-
Found:	68.2%	N_2H_4
	24.99%	Cl^-

D - TRIAMINOGUANIDONIUM SULFATE

Following the procedure described above an attempt was made to prepare triaminoguanidonium sulfate.

One-third of a mole of aminoguanidonium bicarbonate was neutralized with one-third mole of sulfuric acid after which was added two-thirds mole of hydrazine hydrate. The reaction mixture was then heated on the steam bath for a few hours. Upon allowing the water to evaporate no crystals of any kind could be obtained, even with cooling. Finally a pink viscous liquid was formed which when cooled with an ice-salt mixture produced a mass of micro crystals which were filtered with difficulty. The material was very soluble and could be recrystallized only from a 50% alcohol-water mixture. The product which still had a pinkish color was found to contain approximately 48% $SO_4^{=}$, indicating a compound of probably composition $TAG.H_2SO_4$. The actual yield was very small.

When the preparation was repeated, the thick syrup was again obtained. With the addition of excess sulfuric acid, however, a white crystalline material was formed which was easily crystallized from water. The product was analyzed for N_2H_4, with the value of

29.66% being obtained as an average of several determinations. This value was obtained by using the factor 3/2.5 described in Section II-A.

Sulfate analyses indicated a percentage of 73.84. However, the hydrazine and sulfate content would not fit any theoretical, possible salt. A sample was then analyzed for total nitrogen and found to contain 22.2%.* The sulfate and nitrogen content indicated a salt of the composition $TAG \cdot 3H_2SO_4$, which would have the following percentage composition:

N_2	21.4 %
N_2H_4	24.14%
$SO_4^=$	72.5 %

If the factor 3/2.5 is not used, the percentage hydrazine is 24.83, in good agreement with the calculated value. The material melted with decomposition at 240° C.

After solubility determinations had been completed, a marked similarity was noted between the percentages found for this salt and those of hydrazine sulfate. The similarity is shown in the following table.

* Analysis done by Micro-Tech Laboratories, Skokie, Illinois.

	$N_2H_4 \cdot H_2SO_4$	$TAG \cdot 3H_2SO_4$
N_2	21.56%	21.40%
$SO_4^=$	73.85	72.50
N_2H_4	24.67	24.83 (without factor)

X-ray diffraction patterns of the two salts were then made. Since they were identical, it can be stated that the salt presumed to be triamine-guanidonium tri-sulfate was actually hydrazine sulfate.

Because the hydrazine sulfate was so easily precipitated on acidification it was reasoned that very little hydrazinolysis had occurred. Accordingly, when the preparation was repeated, instead of heating on a steam bath, the solution was boiled for one hour with ammonia being liberated as usual in large quantities. After concentrating and cooling, white crystals could be obtained which were filtered and washed with ethanol and ether. This material was analyzed for N_2H_4, and a percentage of 52.7 was obtained, using the factor of 3/2.5. Since the yield was small the preparation was repeated and the crystals obtained were found to contain 52.2% hydrazine. A sulfate analysis of either product indicated 36.36% $SO_4^=$.

All fractions from the two preparations were then recrystallized from an approximately 50% alcohol-water mixture. Repetition of the hydrazine and sulfate analyses showed no change in composition. The percentages indicate a compound containing three TAG molecules and two H_2SO_4 molecules or $3TAG \cdot 2H_2SO_4$. The calculated percentages however are 56.7% N_2H_4 and 37.78% $SO_4^=$. Nitrogen analysis showed 46.51% nitrogen.* Upon drying a sample over barium oxide at 80° C. a loss of weight, presumably water, was found to be 6.25%. This latter determination indicates a possible hydrated salt. If the triaminoguanidonium sulfate were hydrated the calculated percentages would be:

Calculated for $3TAG \cdot 2H_2SO_4 \cdot 2H_2O$		Found
N_2H_4	52.97%	52.23% (with factor)
$SO_4^=$	35.28%	36.32
N_2	46.28%	46.51
H_2O	6.1 %	6.25

The presence of triaminoguanidine was verified by treating a sample of the sulfate salt with the calculated amount of barium nitrate. The barium sulfate was removed by filtration and the filtrate evaporated almost to dryness. Upon cooling, long

* Analysis done by Micro-Tech Laboratories, Skokie, Illinois.

needle-like crystals were obtained which had the characteristic flammability of the triaminoguanidonium nitrate. The x-ray diffraction pattern of the material was identical with that of the known nitrate salt.

If the aminoguanidine, sulfuric acid, and hydrazine mixture is heated at reflux temperature for eighteen hours a white crystalline material can be isolated which is 51.8% hydrazine, using the factor. This material, however, does not appear to have any sulfate present.

The Schotte method of preparation was then tried, treating S-methyl, isothiourea sulfate with the calculated amount of hydrazine hydrate. The reaction mixture was refluxed for three hours and then evaporated under reduced pressure. Upon cooling, a crystalline material was formed which also gave negative results when tested for the sulfate ion.

Another quantity of the thiourea ether was then treated with an excess of hydrazine and the reaction mixture heated only one hour and then concentrated on the steam bath. The material which crystallized out upon cooling was found to contain 51.5% N_2H_4. A portion of this material was

recrystallized from a slowly evaporated water solution. The crystals obtained by this method were found to contain 52.86% hydrazine, with the factor, indicating again the compound $3TAG \cdot 2H_2SO_4 \cdot 2H_2O$. By treating a weighed quantity of this salt with barium nitrate, filtering the barium sulfate, and then evaporating, triaminoguanidonium nitrate was produced. This was again verified by the x-ray diffraction pattern.

From the above series of preparations a number of samples of small yield were obtained. Each sample had at least 52% hydrazine and some detectable sulfate. These preparations were combined and dissolved in a small volume of water and the solution allowed to evaporate slowly. Crystals were formed which could easily be removed, washed and dried. Titration with iodate indicated a percentage hydrazine of 52.34. Further concentration of the filtrate again produced large crystals which contained 52.23% hydrazine.

X-ray diffraction patterns of these recrystallized fractions were identical with the pattern obtained from the first salt of composition $3TAG \cdot 2H_2SO_4 \cdot 2H_2O$.

Triaminoguanidonium sulfate appears to lose its

water of crystallization when heated to 90-95° C. The material then decomposed when heated to 145-150° C. After dehydration a sample of the sulfate salt melted with decomposition in the range of 150-155° C.

Attempts were also made to prepare triaminoguanidonium sulfate, using the double decomposition reaction of silver sulfate with triaminoguanidonium bromide. First, a hot suspension of silver sulfate was added to a warm solution of the bromide salt. There was a violent evolution of gas and the mixture bubbled over the sides of the beaker. When the reaction had subsided, evidence could be seen of silver reduction. After several hours the beaker was coated with a silver mirror.

The reaction was then run in the cold with the silver sulfate being added to a cold solution of the bromide salt. The slurry was then stirred three hours at the end of which time the precipitate had turned completely black. The mixture was then filtered and upon concentrating and cooling the filtrate a mass of white crystals was obtained. These were found to contain 50% hydrazine, but only 8% sulfate. The x-ray diffraction pattern for this material was identical with that of the original bromide salt. The reaction evidently had taken place to only a slight extent.

PROPERTIES

III - PROPERTIES

A - Solubility Determinations

1. Experimental Procedure

In order to determine the solubilities of the triaminoguanidonium salts, saturated solutions were prepared in all-glass system fitted with a stirrer, thermometer, and an exit port for withdrawal of samples and the addition of water, as needed. All joints were ground glass.

The solubility samples were suspended in a water bath maintained at constant temperature, within 0.2° C., by a mercury regulator switch and an electronic relay.

After sufficient time for equilibrium to be attained, at least three hours at the desired temperature, a sample of the saturated solution was withdrawn, placed in a tared 100 ml. volumetric flask and weighed. In all cases excess solute was present. After diluting to the mark, aliquots were analyzed for either anion or cation content. From the data thus obtained, the solubility of the salt was easily calculated and expressed as grams of salt per 100 g. of solvent.

2. Triaminoguanidonium Chloride and bromide

In determining the solubilities of these salts the aliquots were analyzed for halide content. Analysis for N_2H_4 was not done in order to eliminate using the factor described in Section II-A. Titrations using silver nitrate and an absorption indicator were not successful in that a definite end-point could not be observed. The Mohr titration was then tried but the triaminoguanidine was evidently oxidized by the dichromate ion and again no end-point could be obtained. In the Volhard method, the sample solution slowly became colored long before the end-point.

The method finally used to determine the anion concentration, from which the solubilities were calculated, was a potentiometric precipitation titration, using a Cenco line-operated pH meter, with a platinum and a silver, silver-chloride electrode. Potential measurements were taken in the usual manner, titrating with silver nitrate solution. Plots were then made of $\Delta E/ml$ in order to get the well known, maximum differential curve. The silver nitrate solution which was used had been previously standardized against C.P. sodium chloride, using the potentiometric method.

The results are listed in Tables I and II, and graphically in Figure I.

TABLE I

Solubility of triaminoguanidonium bromide in water

Temperature C°	Grams of TAG·HBr per 100 g. water
16.0	4.37
21.7	5.51
30.1	7.63
39.7	10.74
45.5	13.48
50.0	15.48
57.0	19.50
61.8	22.79

TABLE II

Solubility of triaminoguanidonium chloride in water

Temperature C°	Grams of TAG·HCl per 100 g. water
19.0	8.8
22.8	9.87
25.0	10.10
28.9	11.69
36.0	14.53
40.7	16.61
46.0	18.87
47.0	19.56
50.0	21.06
53.0	22.71
53.8	23.23
60.0	26.86

3. Triaminoguanidonium nitrate

In determining the solubility of the nitrate salt, the aliquots were analyzed for hydrazine content according to the method described in Section II-A. The potassium iodate solution was prepared from C.P. potassium iodate and standardized against hydrazine sulfate which had been doubly recrystallized. The results are shown in Table III and Figure I.

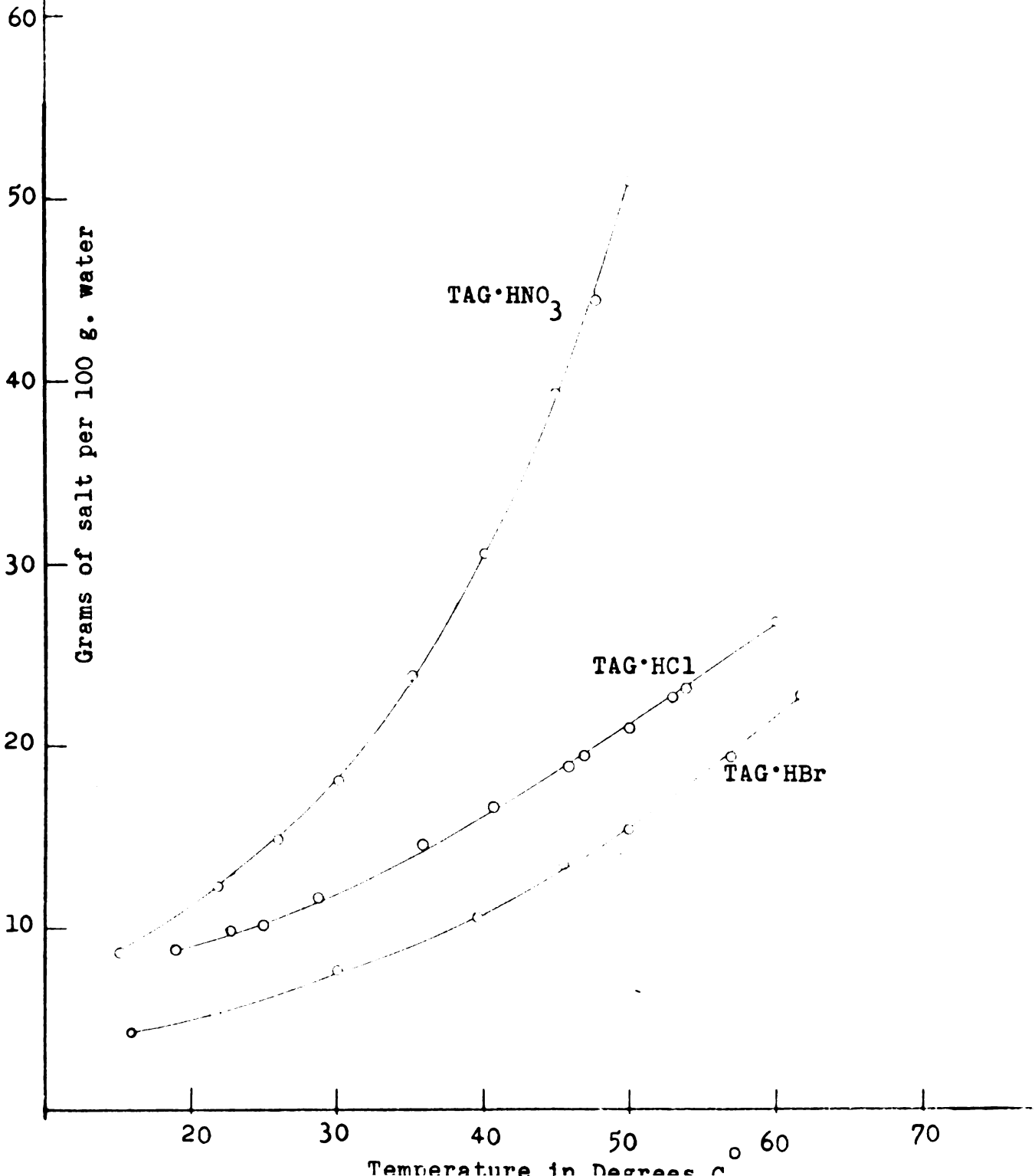
TABLE III

Solubility of triaminoguanidonium nitrate in water

Temperature C°	Grams of TAG·HNO_3 per 100 g. water
15.1	8.65
21.8	12.34
25.9	14.8
30.1	18.13
35.1	23.92
40.0	30.66
45.0	39.43
47.6	44.61
50.0	50.98

FIGURE I

SOLUBILITY OF TRIAMINOGUANIDONIUM SALTS



4. Hydrazine Sulfate

As mentioned in Section II-D, the solubility of a salt believed to be triaminoguanidonium sulfate was determined for water and 1.008 normal sulfuric acid solution. This salt was proven to be hydrazine sulfate. The solubility data was recalculated on this basis with the results being listed in Table IV and shown graphically in Figure II.

The solubilities of hydrazine sulfate in water agree with those reported in the literature.[10]

TABLE IV

Solubilities of Hydrazine Sulfate

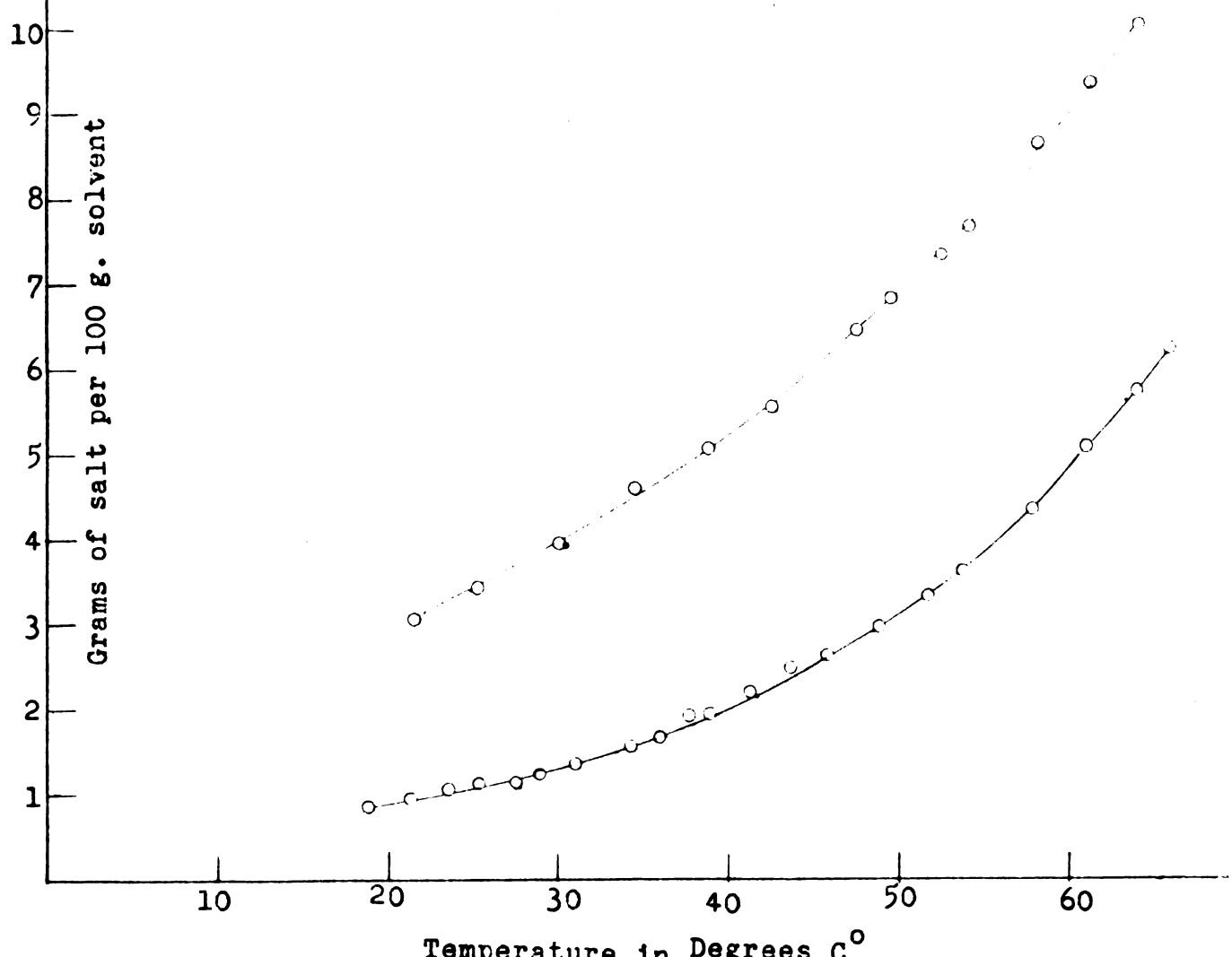
Temperature C°	Grams per 100 g H_2O	Temperature C°	Grams per 100 g acid
21.5°	3.06	18.8°	0.87
25.1	3.42	21.3	0.92
30.1	3.94	23.5	1.06
34.5	4.60	27.5	1.11
38.9	5.08	28.8	1.21
42.5	5.57	31.0	1.35
47.5	6.49	34.3	1.55
49.5	6.83	36.0	1.69
52.5	7.38	37.7	1.90
54.1	7.68	38.8	1.95
58.3	8.67	41.3	2.20
61.2	9.39	43.6	2.50
64.0	10.04	45.7	2.62
		48.8	2.99
		51.6	3.32
		53.7	3.61
		57.9	4.34
		61.0	5.08
		64.0	5.74
		65.9	6.22

FIGURE II

SOLUBILITY OF HYDRAZINE SULFATE

Upper Curve - Water

Lower Curve - 1.008 N H_2SO_4



B - X-ray Diffraction Studies

For purposes of identification, x-ray diffraction patterns of the powdered salts were made. Because of the complex nature of the patterns no attempt was made to determine the specific structures of the products. The diagrams were used only for comparative purposes.

The patterns were made on a North American Philips instrument, using Cu, K_α radiation and a Ni filter. Cameras of a 114.59 mm. diameter were used. Exposure times were four hours each, using 35,000 volts and 15 milliamps.

The ten most prominent lines together with their relative intensities are listed in the following tables for each salt. The "d" distance for the Bragg equation was determined from a previously prepared graph.

TABLE V

TRIAMINOGUANIDONIUM NITRATE

Intensity	"d"
W.	7.16
W.	6.4 4
V.W.	5.52
V.W.	4.17
M.	3.78
V.S.	3.30
S.	3.09
W.	2.98
W.	2.88
W.	2.74

TABLE VI

TRIAMINOGUANIDONIUM CHLORIDE
TAG·HCl

Intensity	"d"
S.	6.62
V.W.	5.16
V.W.	4.48
M.	3.72
W.	3.24
S.	3.13
S.	2.90
V.V.W.	2.40
W.	2.30
V.V.W.	1.88

TABLE VII

TRIAMINOGUANIDONIUM BROMIDE
TAG·HBr

Intensity	"d"
V.S.	4.58
S.	4.06
W.	3.36
S.	3.16
V.S.	2.96
M.	2.45
S.	2.36
V.W.	2.31
W.	1.78
W.	1.64

TABLE VIII

TRIAMINOGUANIDONIUM SULFATE
$3TAG \cdot 2H_2SO_4 \cdot 2H_2O$

Intensity	"d"
M.	8.54
W.	5.64
W.	5.28
W.	5.05
S.	4.75
M.	4.56
W.	4.40
W.	4.18
S.	3.66
V.S.	3.27

C - Study of Di-Acid Salts

Since di-acid salts of aminoguanidine and diaminoguanidine can be prepared it was assumed that multi-protonated salts of triaminoguanidine could also be prepared.

1. Preparation

The procedure for the preparation was the same as previously described in Section II-A, except that an extra mole of the desired acid was added. The material subsequently obtained by evaporation and cooling was very similar to the mono-acid salts. For quick identification, x-ray diffraction patterns were made. The patterns of the supposed di-acid salts were in each case identical with those of the mono-acid salts.

During an investigation of arsenic-organic compounds[9], August Albert in Germany reported the preparation of materials containing a C=O group, not in a ring, by condensation with compounds containing several hydrazine groups. One of these compounds was reportedly triaminoguanidonium dinitrate. No reference, however, is made to the preparation of the triaminoguanidine salt.

2. Neutralization Curves

Tenth-molar solutions of the mono-acid and supposedly di-acid salts of triaminoguanidine were prepared. Ten milliliter samples in 100 ml. of water were then titrated with 0.0891 N. NaOH solution. The changes in pH were followed by a line-operated Cenco Titration pH Meter, using a saturated calomel and glass electrode. These changes were plotted as usual and from the plot of pH versus volume of alkali it is evident that the mono-acid salts had no titratable proton. It is also evident that the di-acid salts were actually mono-acid.

Ten milliliters of tenth-molar triaminoguanidonium sulfate were also diluted with 100 ml. of water and then titrated with 0.1 N sodium hydroxide. The resulting curve has the appearance of a buffering action. This might be expected since the triaminoguanidonium ion $TAGH_2^{++}$ would act as a weak acid.

FIGURE III

TITRATION CURVES OF
TRIAMINOGUANIDONIUM NITRATES

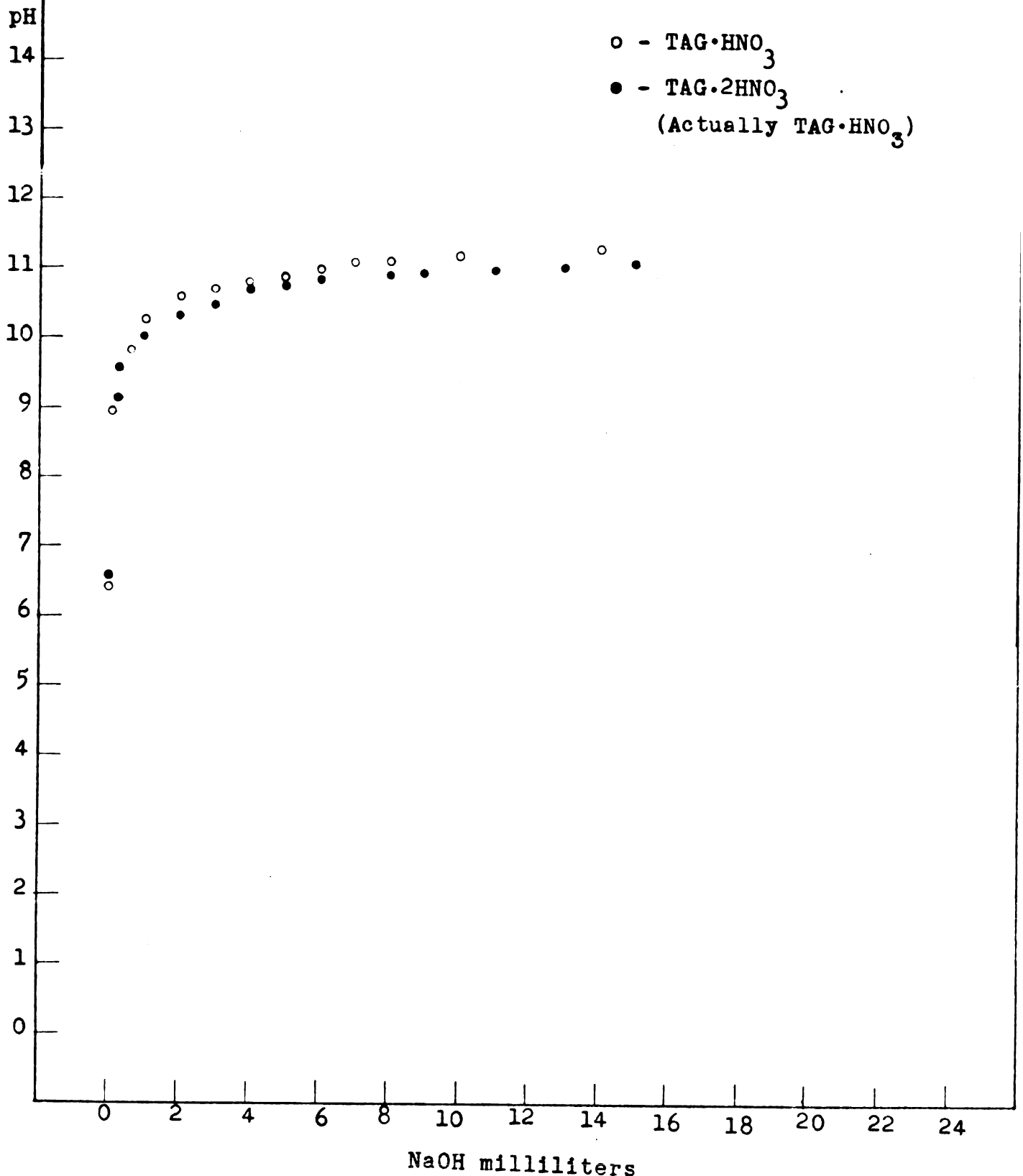


FIGURE IV

TITRATION CURVES OF
TRIAMINOGUANIDONIUM BROMIDES

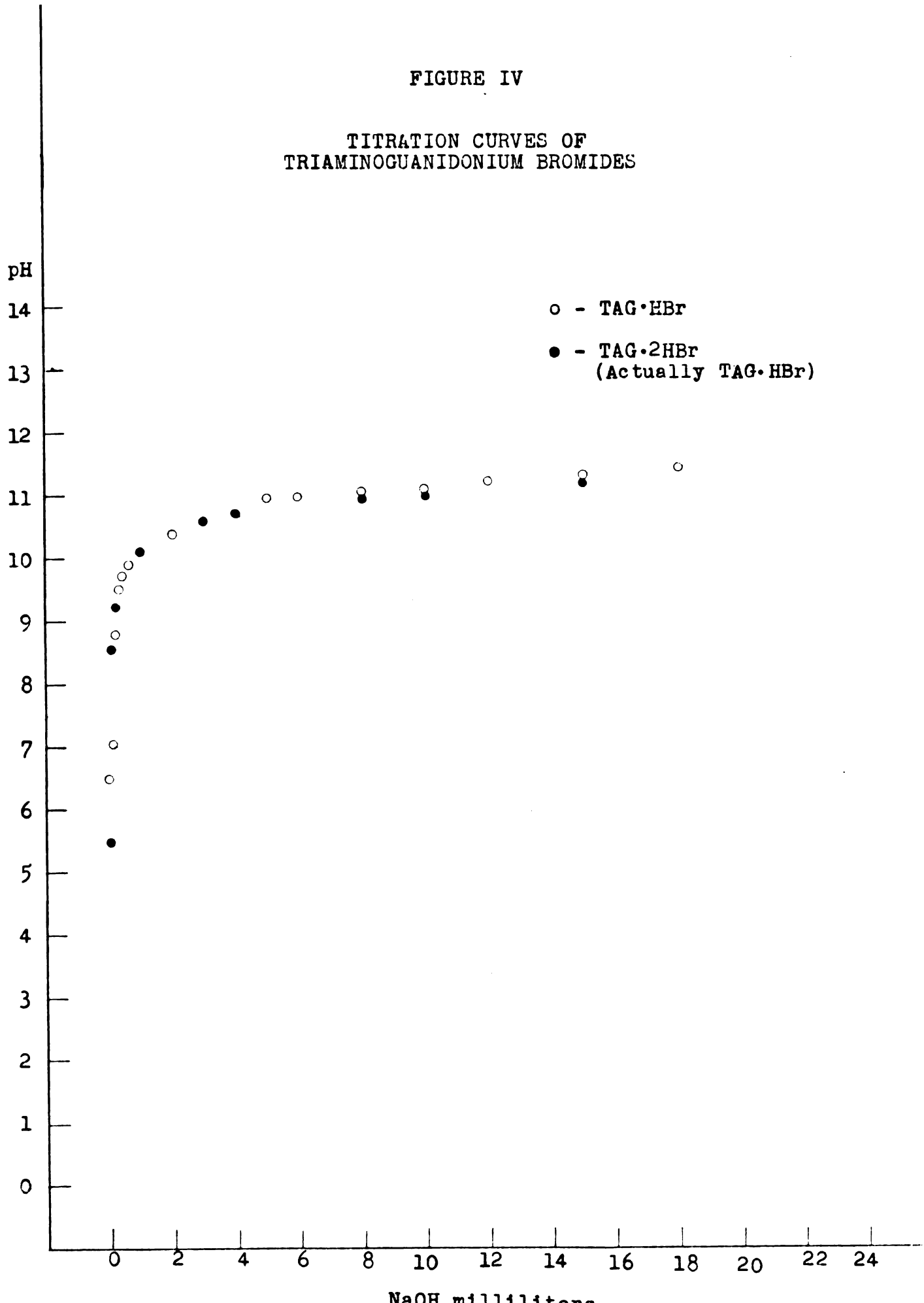


FIGURE V

TITRATION CURVES OF
TRIAMINOGUANIDONIUM CHLORIDES

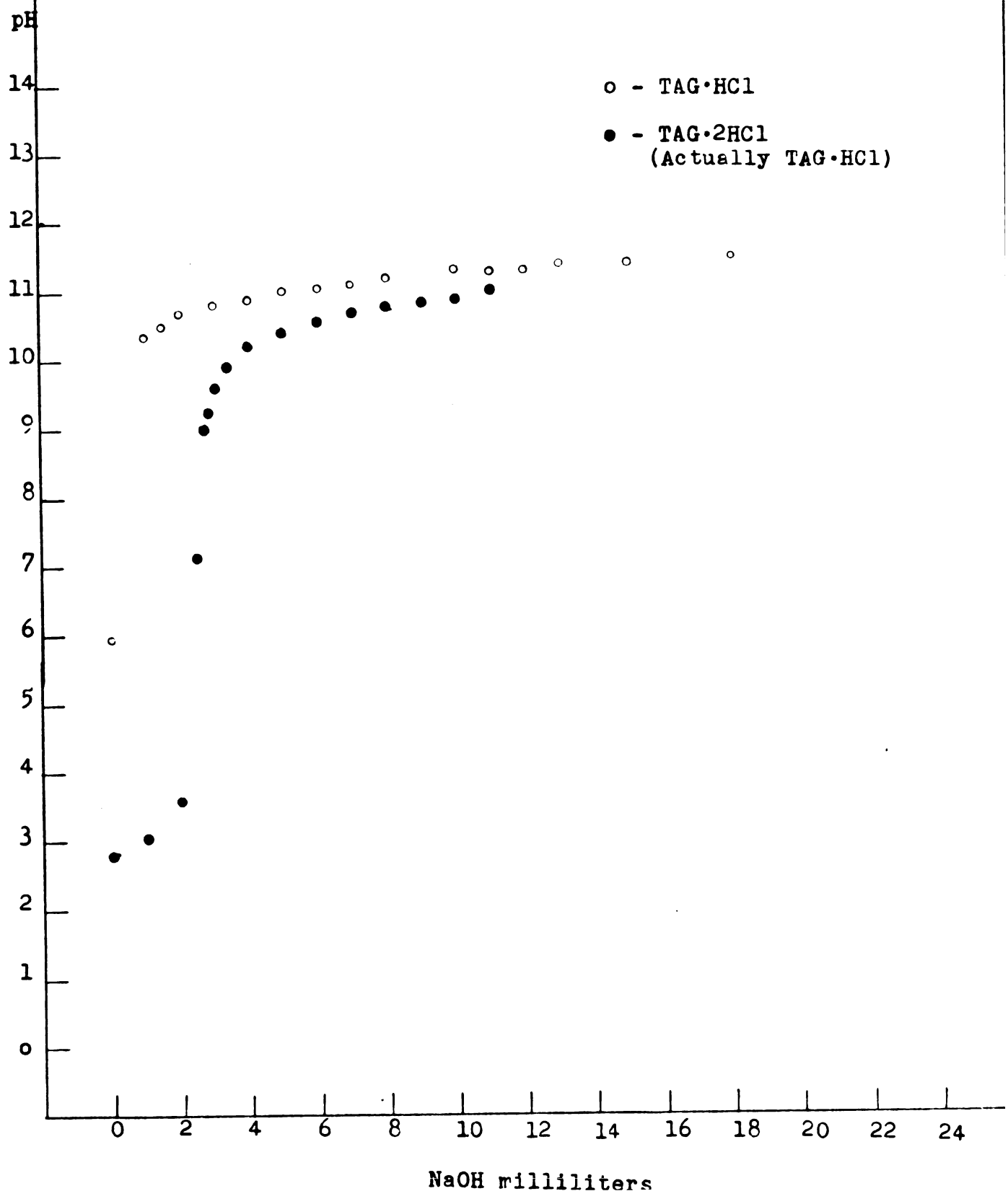
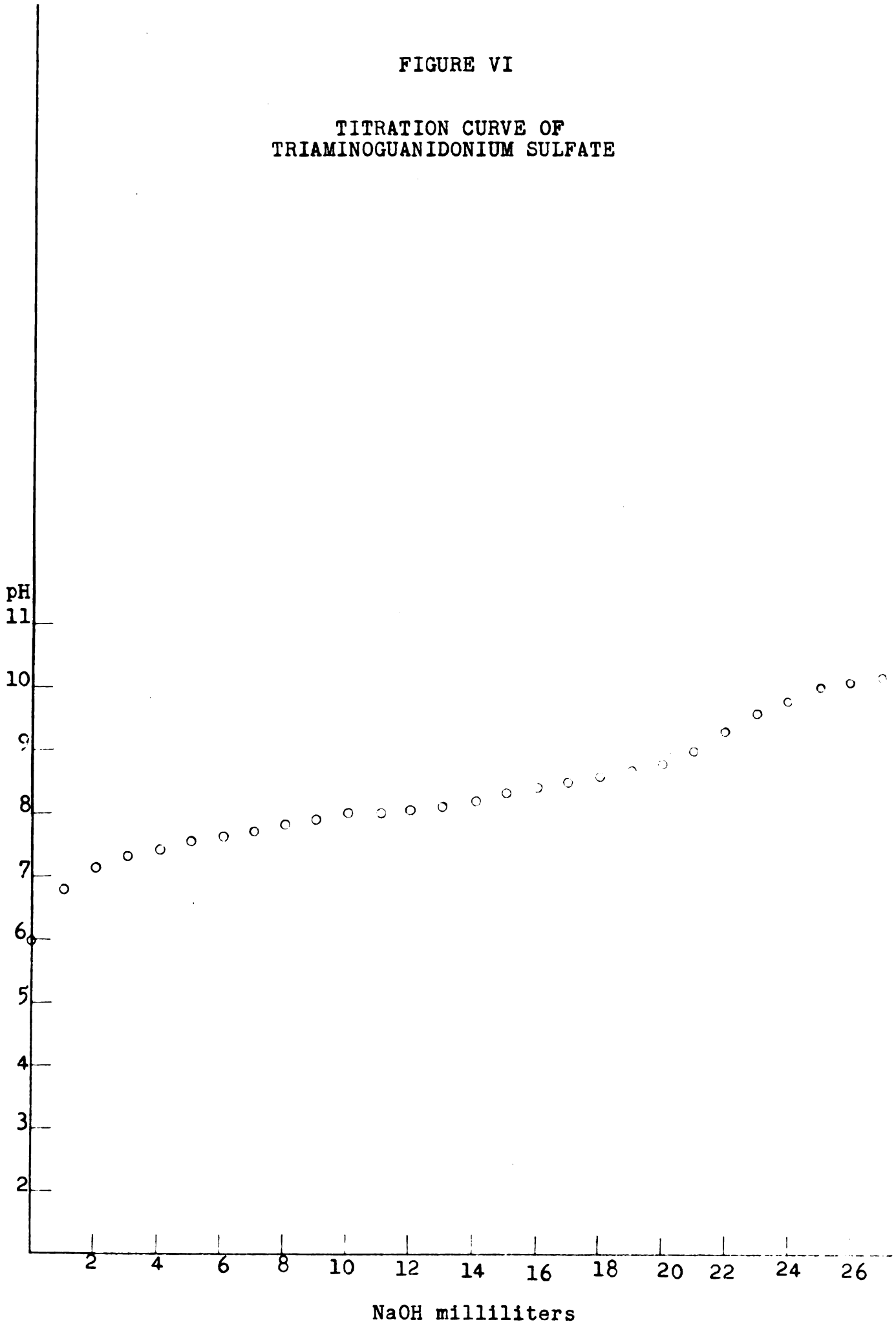


FIGURE VI

TITRATION CURVE OF
TRIAMINOGUANIDONIUM SULFATE



DISCUSSION

IV - DISCUSSION

The nitrate, chloride and bromide salts of triaminoguanidine can be easily prepared by the hydrazinolysis of aminoguanidine. These salts are stable in water or acid solutions. Only the monoprotonated salts could be prepared and titrations with base indicate that the salts do not act as "acids" in water solution.

The difficulties and reactions encountered in preparing triaminoguanidonium sulfate were described in Section II-D. These difficulties require some explanation. The sulfate salt finally isolated had the composition $3TAG \cdot 2H_2SO_4 \cdot 2H_2O$; if a solution of this material is acidified with sulfuric acid hydrazine sulfate is formed and precipitates in white crystals which are easily filtered. Evaporation and cooling of the filtrate produces a crystalline material which can be identified as aminoguanidonium sulfate. This reaction might be expressed as an equilibrium as shown below:

$$2AGH_2SO_4 + 4N_2H_4 \rightleftharpoons 2(TAG\ H_2SO_4) + 4NH_3$$

$$\downarrow\uparrow$$

$$(TAG)_2\ H_2SO_4 + H_2SO_4$$

Thus crystallization of an equimolar mixture of the two different salts would produce a material which upon analysis would agree with a compound of composition $3TAG \cdot 2H_2SO_4 \cdot 2H_2O$. Addition of base would then favor formation of the compound $(TAG)_2H_2SO_4$, liberating in the process one mole of sulfuric acid. A solution of the salt $3TAG \cdot 2H_2SO_4 \cdot 2H_2O$ would then be expected to be acidic and this is actually the case. A hundredth-molar solution has a pH of six and titration with base (sodium hydroxide) indicates neutralization at a molar ratio of two moles base/one mole salt, as would also be expected. The low melting point of the triaminoguanidonium sulfate also indicates that the material is probably not a pure compound.

The pH of a triaminoguanidonium sulfate solution can be considered as due to the following dissociation:

$$TAGH_2^{++} \rightleftharpoons TAGH^{+} + H^{+}$$

Choosing three different points on the titration curve and applying the buffer equation, $H^+ = \frac{C_a}{C_s} K_a$, gives the following results for apparent K_a and pK_a of this dissociation:

K_a	pK_a
2.1×10^{-8}	8.32
2.0×10^{-8}	8.30
2.4×10^{-8}	8.38

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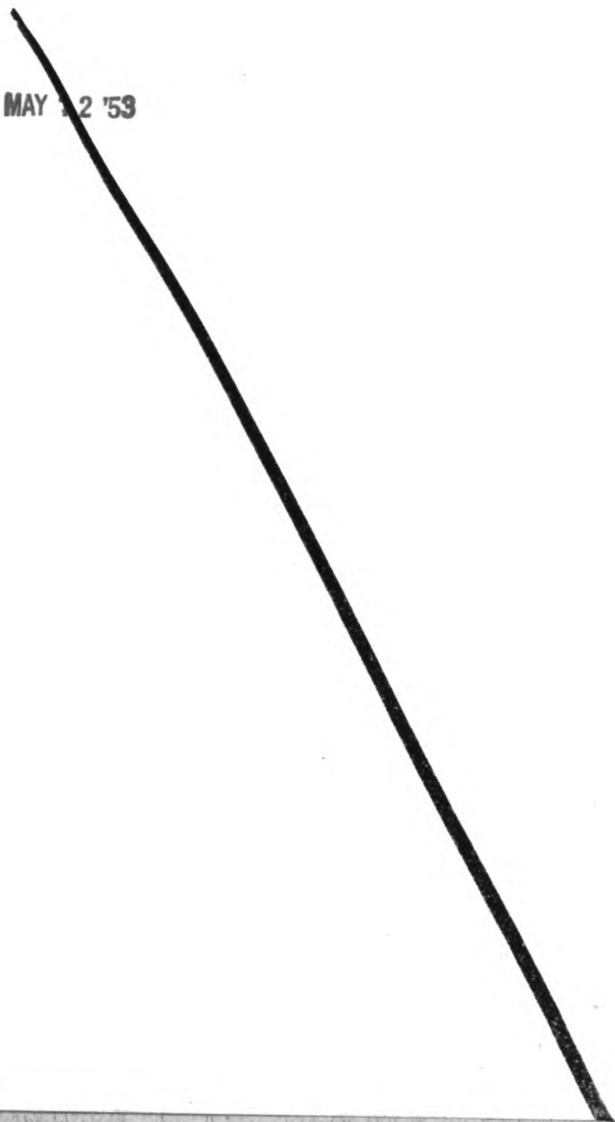

ABSTRACT OF A THESIS

by

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"PREPARATION AND CHARACTERIZATION OF SALTS OF TRIAMINOGUANIDINE"

Current interest in the uses of hydrazine and other high nitrogen content compounds has prompted a more detailed study of the salts of triaminoguanidine. The purpose of the research was to prepare several salts of triaminoguanidine and study their characteristics.

The chloride, bromide, nitrate and sulfate salts were prepared by the hydrazinolysis of the corresponding aminoguanidine salts. Triaminoguanidonium sulfate was also prepared by the hydrazinolysis of S-methyl isothiourea sulfate.

Solubility determinations as a function of temperature were made of the nitrate, chloride and bromide salts in water. The solubility of hydrazine sulfate was determined, both in water and in one normal sulfuric acid.

For purposes of identification, powder x-ray diffraction patterns were made of the salts. The ten most prominent lines of each pattern are listed with their relative intensities and corresponding "d" distances for the Bragg equation.

Attempts were made to prepare di-acid salts of triaminoguanidine. X-ray diffraction studies and titrations with alkali show that only the mono-acid salts can easily be prepared.

From the reactions and properties of triaminoguanidonium sulfate it was deduced that the salt isolated was actually an equimolar mixture of two different compounds which form an equilibrium in neutral water solution.