benzyl bromide with the ketal, Table IV) which could not be cyclized, although the corresponding acetal has been reported (*1*) to cyclize in 56% yield. The visible and ultraviolet absorption spectra of the new acridizinium salts may be found in Table II.

Comparison of the ultraviolet absorption maxima of the monohaloacridizinium derivatives (II) with those observed in the 11-methyl series (IV) is made in Table III. With only one adjustment (noted in the table), there is close correspondence in absorption maxima between the compounds with and without the alkyl group. More remarkable is the effect of the position of the halogen atom on the shift of the maximum observed as halogen is varied from fluorine to iodine. The shift in the 7-halogen series amounts to about 7 mμ, while in the 9-halogen series the shift amounts to 23 mμ.

EXPERIMENTAL

Quaternization and Cyclization. General procedures have been described (*1*). Experimental data have been summarized in Tables IV and V.

Benzyl Iodides. Commercially available benzyl chlorides too unreactive for the quaternization reaction were first converted to the iodide. The benzyl chloride was added to an acetone solution containing a slight excess of sodium iodide and the mixture refluxed for 10 minutes. The solution was filtered, and the acetone removed in vacuo without heat. The residue was dissolved in ether, the solution filtered, and the ether removed in vacuo. The residual benzyl iodide was used immediately in the quaternization reaction.

Conversion of Quaternary Iodides (III) to Chlorides. A tenfold excess of freshly precipitated and washed silver chloride was stirred for six hours with a solution of the iodide (III) in water or methanol. The mixture was filtered and concentrated. The residue was used directly in the cyclization reaction.

Spectra. The ultraviolet absorption spectra were determined in 95% ethanol using a Cary Model 14 spectrophotometer.

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Adsorption Study of Ferrimetaphosphate

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Preparation methods for an active ferric metaphosphate are given, and the optimum method is noted. The ferrimetaphosphate has a very high capacity for water adsorption and can be regenerated with small amounts of energy. The ferrimetaphosphate has a high capacity for adsorption of ammonia; however, the ammonia is taken up irreversibly and the absorbent is converted into an inactive material. Static water and ammonia adsorption values show that the specific surface is large; about 640 sq. meters per gram for a monomolecular layer. From the data, an estimation is made that the adsorbed layer of water molecules surrounding the compound is about 8 molecules thick.

ADDITION of a solution of sodium polyphosphate glass to an aqueous solution of a ferric salt precipitates ferrimetaphosphate which exhibits adsorptive behavior toward water and ammonia. By careful attention to the method of preparation, a solid with a large specific surface can be obtained. The results of such an investigation are reported here.

PREPARATION

Direct Method. A solution of $(NaPO_3)_n$ was prepared by dissolving 30.5 grams of R-S Unadjusted Calgon in rapidly stirred water, total volume 100 ml. End group titrations indicated an average chain length of 9. The formula weight of the glass was chosen as 612, thus, such solutions can be referred to as $0.5M$. With continuous stirring, the solution of the phosphate glass was added to a freshly prepared $0.5M$ ferric chloride solution until the flocculent, yellow precipitate which first formed changed to a fine, white precipitate. The total addition of phosphate was kept

Table I. Effect of Preparation Variables on Activity of Ferrimetaphosphates

Condition	H_2O Adsorbed, Mg./G. (Relative Humidity, 100%)
$0.2M$ $FeCl_3$ *vs.* $0.5M$ $(NaPO_3)_n$	90.0
Both solutions $0.25M$	116.8
Both solutions $0.5M$	132.5

All were dried to constant weight before being placed in atmosphere for 4 hours.

Table II. Effect of Drying on Activity of Ferrimetaphosphate

Drying Treatment at 108 ± 2° C.	H_2O Adsorbed, Mg./G. (Relative Humidity, 100%)
Dried to constant weight	197.5
Dried 1½ hours	274.5
Dried 1 hour	344.0

All samples prepared by direct method using $0.5M$ solutions; samples in atmosphere for 12 hours.

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Table III. Effect of Aging on Activity of Air Dried Ferrimetaphosphate

Condition	NH_3 Adsorbed, Mg./G.
24 hours	71.80
3 days	33.40
3 weeks	11.65

Sample air dried, then stored in closed bottle in desiccator over $CaSO_4$.

Table IV. Effect of Aging on Activity of Oven Dried Ferrimetaphosphate

Condition	H_2O Adsorbed, Mg./G. (Relative Humidity, 100%)
Sample oven dried 1½ hours, then aged 2 weeks, then dried to constant weight	63.0
Sample oven dried 1½ hours, then aged 13 months, no further drying	73.8

Samples in atmosphere for 12 hours.

Table V. Representative Analysis of Ferrimetaphosphate

Fe_2O_3, %	P_2O_5, %	H_2O %	Conditions
	Calculated		
26.48	58.74	14.78	
	Experimental		
26.80	57.95	14.01	Direct, 0.5*M* solutions
25.39	51.59	14.50	Indirect, 0.5*M* solutions
26.60	56.63	15.09	Direct, 0.5*M* solutions
24.45	53.16	15.55	Direct, 0.2*M* $FeCl_3$
25.36	49.30	16.25	Direct, both solutions 0.1*M*
26.62	57.65	14.41	Direct, 0.5*M* solutions
26.16	52.24	14.47	Indirect, 0.5*M* solutions
27.25	59.45	15.00	Direct, 0.5*M* solutions

Samples prepared with the direct method and 0.5*M* solutions were more constant in composition as seen in the values listed.

Table VI. Specific Surface, S, of Ferrimetaphosphates

Sample Treatment	H_2O, Mg./G.	S_{H_2O}, Sq. Meters/G.	NH_3, Ml./G.	S_{NH_3}, Sq. Meters/G.
Direct; oven dried to constant weight	197.5	660		
Direct; oven dried to constant weight	193.0	644		
Indirect; oven dried to constant weight	244.3	815		
Direct; oven dried 1½ hours	274.5	916	161.0	629
Direct; oven dried 1 hour	344.0	1145	161.8	635
Direct; air dried			191.0	746
Direct; desiccator dried over $CaSO_4$			164.2	643

at slightly less than 3.0 moles of $(PO_3)^-$ groups per mole of iron, because of the complexing action of the polyphosphate on iron. Care was taken to avoid an excess of polyphosphate by testing for complete precipitation of the iron using KCNS. After filtering, the precipitate was dispersed in water only once because of its pronounced tendency to peptize. It was then redispersed in dioxane three or four times, and after each dispersion the filtrate was tested for the presence of sodium and chloride. The precipitate was allowed to dry in the air on porous plates for 24 hours.

Indirect Method. Addition of excess polyphosphate to the precipitate from the direct method caused it to dissolve, giving a clear solution with a faint pink tinge. A flocculent, pinkish mass came out of the solution on the addition of dioxane. This mass was redissolved in water, and when this latter solution was added to a ferric chloride solution, a fine, white precipitate was again obtained. From this point, the washings were carried out as in the direct method.

The analyses of the ferrimetaphosphates obtained in the direct method showed they were more constant in composition than the ferrimetaphosphates from the indirect method. The former were also better adsorbents. Use of less concentrated solutions in the direct method affected the activity of the ferrimetaphosphates (Table I).

Residual solvent was removed by heating in an oven at 108 ± 2° C. for an hour or by placing the ferrimetaphosphate in a desiccator over $CaCl_2$ or $CaSO_4$ for 48 hours. Desiccation of the adsorbent to constant weight by oven drying diminished the activity of the surface (Table II).

Aging of the air dried precipitate diminishes the activity of the ferrimetaphosphate for ammonia adsorption (Table III). However, aging of the ferrimetaphosphate after oven drying does not diminish its activity for water adsorption (Table IV).

CHEMICAL ANALYSIS

In Table V, the calculated values for basic ferrimetaphosphate, $Fe(OH)_{0.5}(PO_3)_{2.5}$ are compared with some of the experimental results by the different methods of preparation. The iron(III) was analyzed by the conventional dichromate technique; the phosphorus, by an ion exchange method (*6*) or by the volumetric determination of the precipitate of ammonium phosphomolybdate in a solution of standard alkali as given by Hillebrand and coworkers (*4*); the water, by measuring the loss of weight after ignition in a furnace between 700° to 800° C.

PROPERTIES

Water Adsorption and Ammonia Adsorption. Adsorption of water and ammonia gas was studied in static systems. Water adsorption was measured by placing weighed samples for stated times in an atmosphere of constant relative humidity, following a procedure of Clarke, Groth, and Duzak (*2*). The water adsorbed was determined as the gain in weight of the sample. Ammonia adsorption was studied volumetrically (*5*).

Table VII. Adsorption at Varying Relative Humidities

	P/P_0					
Sample 1	0.310	0.520	0.712	0.793	0.880	1.000
Mg./g.	57.1	63.0	109.0	135.0	164.0	197.5
$v(L.\ STP)$	0.0709	0.0783	0.1355	0.1680	0.2048	0.2458
$P/v(P_0 - P)$	6.12	13.38	18.50	23.18	29.75	...
Sample 2						
Mg./g.	56.9	53.5	92.5	143.0	164.0	193.0
$v(L.\ STP)$	0.0708	0.0667	0.1152	0.1780	0.2042	0.2420
$P/v(P_0 - P)$	6.12	15.65	21.70	21.85	30.18	...

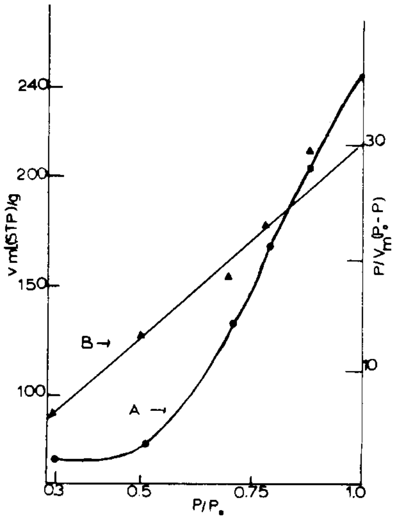

Figure 1. Adsorption isotherm
A → H_2O by sample 1
B → BET values for sample 1

Table VIII. Adsorption–Desorption of Water (Mg. H_2O/Gram Adsorbent)

	Cycle 1		Cycle 2	
	100% RH	50% RH	100% RH	50% RH
	Sample A			
Ads.	132.5	51.0	72.6	32.1
Des.	33.7	10.3	14.4	7.8
% Des.[a]	25.4	20.3	8.4	10.7
	Sample B			
Ads.	90.0	47.1	62.5	19.9
Des.	13.5	0.0	22.2	5.1
% Des.[a]	15.0	0.0	16.0	7.6
	Sample C			
Ads.	197.5	63.0	142.8	28.8
Des.	41.4	11.6	100.8	17.3
% Des.[a]	21.0	18.4	33.7	21.6
	Sample D			
Ads.	279.1	73.8	189.4	41.4
Des.	122.9	27.1	135.5	46.7
% Des.[a]	44.0	36.7	39.2	53.0

Treatment of samples:
A and C, direct method, both solutions 0.5*M*; oven dried to constant weight. B, direct method, 0.2*M* $FeCl_3$ *vs.* 0.5*M* $(NaPO_3)_n$; oven dried to constant weight. D, direct method, solutions 0.5*M*; oven dried 1½ hours; aged 13 months.
Conditions of cycling:
Adsorption time: A and B = 4 hours; C and D = 12 hours.
Desorption time: ½ hour; desorption pressure approximately 0.1 atm.; temperature = 24 ± 2° C.
[a] Per cent desorbed is calculated on total amount present on the adsorbent.

Results for the specific surface of the ferrimetaphosphates assuming a monomolecular layer are given in Table VI. The cross-sectional area of the water molecule was taken as 10.0 A^2, that of the ammonia molecule, 14.6 A^2 (*3*). Samples 1 and 2 which were prepared a month apart are included in Table VI to show the consistency of ferrimetaphosphates prepared by the direct method and then dried to constant weight. Gregg (*3*) has pointed out the importance of being able to prepare a solid with a reproducible specific area by close attention to concentration, rate of mixing, etc.

Experiments were run on the first two samples of Table VI using varying relative humidities. The isotherms from these values are of the Type II, and hence the BET equation could be applied (*1*). The data are summarized in Table VII and graphed in Figures 1 and 2. For sample 1, the specific surface by the BET is 87.8 sq. meters per gram; for sample 2, 77.9 sq. meters per gram. From these values and the values obtained by assuming a monomolecular layer, we estimate that the adsorbed layer is about 8 water molecules thick.

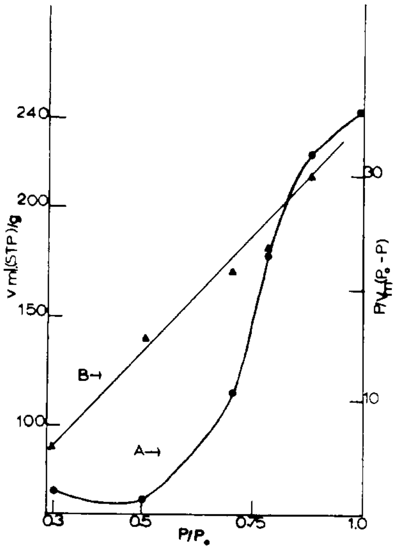

Figure 2. Adsorption isotherm
A → H_2O by sample 2
B → BET values for sample 2

Table IX. Cycling Performance of Sample D

	100% RH			50 % RH		
Cycle	A	D	% D	A	D	% D
1	279.1	122.9	44.0	73.8	27.1	36.7
2	189.4	135.5	39.2	41.4	46.7	53.0
3	101.7	120.3	38.6	56.5	39.2	40.0
4	202.2	128.9	32.8	46.7	38.4	36.4

Conditions same as given in Table VIII for Sample D.

The nature of the adsorption taking place appears to be physical in the case of the water adsorption, for the water could be desorbed using a pump (Table VIII). The data show that the best of several effective and useful H_2O adsorbents is the ferrimetaphosphate prepared by the direct method using 0.5*M* solutions and oven dried at 108 ± 2° C. for 90 minutes. It is reversible to about 40% of the initial adsorption, is regenerated with small amounts of energy (0.1 atm. pressure), and shows good cycling performance (Table IX).

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