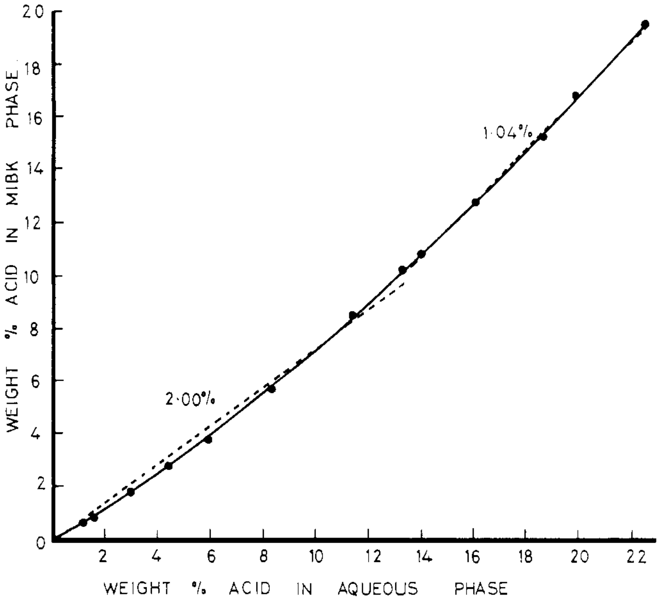

Figure 1. Distribution of acetic acid between water and methyl isobutyl ketone at 28 C. (system AO-14, reference *21*)

experiments is greater than the individual error in either slope.

The use of linearized data is not suitable for every purpose. When careful design is required, it is best to fit curves of higher orders and to do the arithmetic on a computer. This is particularly true when one is interested in nonlinear portions of the equilibrium curve. An error of only 1% in the linearization of the data may lead to as much as say 10% error in the design. Finally, isothermal conditions of operation are implied, and this may not always be so, especially in the case of gas absorption.

## NOMENCLATURE

$b$ = slope of line passing through $\bar{x}$, $\bar{y}$
$m$ = slope of line passing through origin
$n$ = number of experimental points
$x, y$ = concentrations
$\bar{x}$ = arithmetic mean of $x$ values
$\bar{y}$ = arithmetic mean of $y$ values

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# Adsorption of Ferripolyphosphate

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A SUBSTANCE which possesses a surface of 100 to 1000 sq. meters per gram is considered a high-grade adsorber. The authors have prepared iron polyphosphate gels belonging to this class of absorbers. Their high capacity for basic materials, such as water and ammonia, and especially their low regeneration temperature should make them of interest where low heat with relatively high drying efficiency must be maintained.

## EXPERIMENTAL PROCEDURES

**Preparation.** The preparation of these porous white gels has been reported (*4*, *6*). They were obtained by the addition of solutions of sodium polyphosphate glass (30.5 grams of R-S unadjusted Calgon in 100 ml. of water), having the general formula $Na_{n+2}P_nO_{3n+1}$ and an average of nine phosphorus atoms per chain, to 0.5*M* iron (III) salt solutions. The gels were desiccated by washings with dioxane before drying in an oven. Analysis of the gels gave a molar $Fe_2O_3$-$P_2O_5$ ratio of 0.41. This ratio is equivalent to the

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**The cycling performance of ferripolyphosphate gels for water adsorbed at room temperature from 18 and 31% relative humidity has been studied at a constant regeneration pressure of 0.1 atm. and temperatures of 45°, 65°, and 120° C. The amount of water adsorbed by gels regenerated at 120° C. was about 50% greater than gels regenerated at 45° C.; while the percentage of water desorbed at 120° C. was about 100% greater than that desorbed at 45° C. The capacity of the gels for ammonia adsorption increased with aging.**

substitution of an iron (III) atom for three sodium atoms in the phosphate chain ($Na_2O$–$P_2O_5$ molar ratio 1.22, empirical formula $Na_{11}P_9O_{28}$) to give the empirical formula $Fe_{11}P_{27}O_{84} \cdot nH_2O$. The value of $n$ varies with the drying procedures.

**Adsorption.** Water was adsorbed in a static system at room temperature (*2*) (22–25° C.). Samples were placed in small weighing bottles in a desiccator containing a saturated solution of $CaCl_2$ (31% relative humidity), or $KC_2H_3O_2$ (18.7% relative humidity) for a 12-hour period. After adsorption, the samples were removed from the humidity atmosphere, weighed, and desorbed in a heated vacuum desiccator. To study ammonia adsorption volumetrically, a modified nitrometer was constructed from a 50-ml. buret (*7*). In some runs, the amount of $NH_3$ adsorbed on the sample was also determined by the Kjeldahl method (*5*).

Table I. Cycling Performance of Ferripolyphosphate for Water Adsorption

| | 18% RH | | | 31% RH | | |
|---|---|---|---|---|---|---|
| Cycle | A | D | %D | A | D | %D |
| [a]1 | 18.0 | 10.1 | 56.1 | 20.2 | 11.8 | 58.4 |
| 2 | 10.1 | 8.4 | 46.7 | 11.3 | 9.4 | 47.7 |
| 3 | 8.4 | 8.4 | 46.7 | 9.9 | 9.9 | 49.0 |
| 4 | 8.9 | 7.8 | 42.2 | 10.3 | 9.4 | 54.6 |
| 5 | 7.8 | 7.3 | 39.5 | 9.4 | 8.0 | 38.8 |
| 6 | 7.8 | 8.4 | 44.2 | 8.9 | 9.4 | 43.7 |
| 7 | 8.4 | 7.8 | 41.1 | 9.4 | 8.9 | 41.4 |
| 8 | 10.1 | 10.6 | 49.8 | 11.3 | 11.8 | 49.4 |
| 9 | 8.9 | 8.4 | 42.9 | 9.4 | 9.4 | 43.7 |
| 10 | 8.4 | 9.5 | 48.5 | 9.9 | 11.3 | 51.4 |
| [b]1 | 18.9 | 12.0 | 63.5 | 20.7 | 14.5 | 70.0 |
| 2 | 10.6 | 10.1 | 57.7 | 12.4 | 10.9 | 58.6 |
| 3 | 12.9 | 13.8 | 68.0 | 14.5 | 16.1 | 72.5 |
| 4 | 15.2 | 16.1 | 74.2 | 16.1 | 17.1 | 77.0 |
| 5 | 14.3 | 18.4 | 92.5 | 16.6 | 21.2 | 97.7 |
| 6 | 18.9 | 13.8 | 67.6 | 21.8 | 19.2 | 86.1 |
| 7 | 18.4 | 17.5 | 70.0 | 19.7 | 19.7 | 86.4 |
| 8 | 15.2 | 13.8 | 60.8 | 22.8 | 15.5 | 59.8 |
| 9 | 11.1 | 13.4 | 67.0 | 10.9 | 11.9 | 55.9 |
| 10 | 18.0 | 17.1 | 69.5 | 18.1 | 17.6 | 64.0 |
| [c]1 | 26.5 | 30.6 | 100 | 23.9 | 25.7 | 100 |
| 2 | 29.8 | 29.9 | 100 | 25.7 | 28.5 | 100 |
| 3 | 28.9 | 28.2 | 97.6 | 30.9 | 34.2 | 100 |
| 4 | 26.5 | 32.2 | 100 | 32.8 | 36.6 | 100 |
| 5 | 28.2 | 26.5 | 94.0 | 34.7 | 33.3 | 96.0 |
| 6 | 29.8 | 30.6 | 100 | 36.1 | 36.1 | 96.3 |
| 7 | 27.4 | 31.4 | 100 | 32.3 | 39.0 | 100 |
| 8 | 30.6 | 27.4 | 89.5 | 36.6 | 35.7 | 97.5 |
| 9 | 27.4 | 29.8 | 97.4 | 33.8 | 35.7 | 100 |
| 10 | 25.7 | 24.1 | 90.9 | 31.4 | 30.9 | 98.4 |

[a] 45 ± 2° C.; [b] 65 ± 2° C.; [c] 120 ± 2° C.

A = $H_2O$ adsorbed, mg./gram gel.

D = $H_2O$ desorbed in vacuo at specified temperatures, mg./gram gel.

Time: adsorption, 12 hours in constant relative humidity; desorption, $\frac{1}{2}$ hour in vacuum desiccator; pressure = 0.1 atm.

%D = per cent desorbed is calculated on total amount present on adsorbent.

## RESULTS AND DISCUSSION

The data (Table I) show that the ferripolyphosphate gels prepared by the authors' methods are easily and repeatedly activated under mild conditions of 0.1 atm. pressure. Further improvement in cycling over that previously reported (*4*) was obtained by vacuum drying at low regeneration temperatures. The data also show that the adsorptive capacity of the gels does not drop off with an increase in regeneration temperatures. At a constant regeneration pressure of 0.1 atm., an increase in regeneration temperature from 45° to 65° to 120° C. increased the average amount of water adsorbed per gram at room temperature and 18% RH from 18 mg. to 21 mg. to 28 mg. The percentage of water desorbed under these conditions increased from 45 to 70 to 100%. Similar results were obtained at 31% RH. In the earlier study (*4*) at a regeneration pressure of 0.1 atm. and 25° C., the gel adsorbed about 30% of its own weight of water from 100% RH. Under these conditions about 40% of the water had been desorbed in each cycle.

An ideal drying agent should have constant volume and shape; and should not become sticky on handling (*8*). The authors' ferripolyphosphates possess these good qualities when water is adsorbed, but anomalous behavior is observed when ammonia is the adsorbate. Data of Table II sum-

Table II. Effect of Aging and Drying on Adsorptive Behavior for Ammonia

| Sample | Treatment | $NH_3$, Mg./G. Adsorbed | Observation |
|---|---|---|---|
| 1 | Air dried 24 hours. | 51.6 | Sample melted in tube, becoming red, sticky mass; tube became hot; steam evident on inside of tube. |
| 2 | Air dried 24 hours; aged in closed bottle in desiccator for 6 months. | 69.8 | Sample retained shape; did not become sticky; red color and steam evident in tube. |
| 3 | Air dried 24 hours; dried 24 hours over $CaSO_4$; then aged 2 weeks. | 64.8 | Sample retained shape; more discoloration and heating than in sample 2. |
| 4 | Air dried 24 hours; oven dried $\frac{1}{2}$ hour at 108 ± 2° C. | 64.7 | Sample retained shape; less discoloration and heating than in sample 3. |
| 5 | Air dried 24 hours; dried in heated vacuum desiccator at 58° C. and 0.1 atm. pressure for 2 hours. | 93.3 | Some discoloration and heating; sample retained shape. |
| 6 | Treatment as in sample 4; then aged 6 months in closed bottle in desiccator. | 122.4 | No loss of shape; slight heating and discoloration. |

Table III. Weight Gain in Mg. of $NH_3$ per Gram of Adsorbent

| Sample | Method<br>Volumetric | <br>Kjeldahl | <br>Weighing |
|---|---|---|---|
| 2 | 69.8 | 84.5 | 76.7 |
| 5 | 93.3 | 86.4 | 59.7 |
| 6 | 122.4 | 123.2 | 72.0 |

Table IV. Analysis of Ferripolyphosphate Before and After $NH_3$ Adsorption

| | $Fe_2O_3$, % | $P_2O_5$, % | $H_2O$, % | $NH_3$ % | Molar Proportions, $Fe_2O_3$ : $P_2O_5$ : $H_2O$ : $NH_3$ |
|---|---|---|---|---|---|
| Before | 27.25 | 59.45 | 15.00 | . . . | 1 : 2.5 : 4.9 : |
| After | 24.00 | 53.00 | 12.97 | 8.83 | 1 : 2.5 : 4.8 : 3.5 |

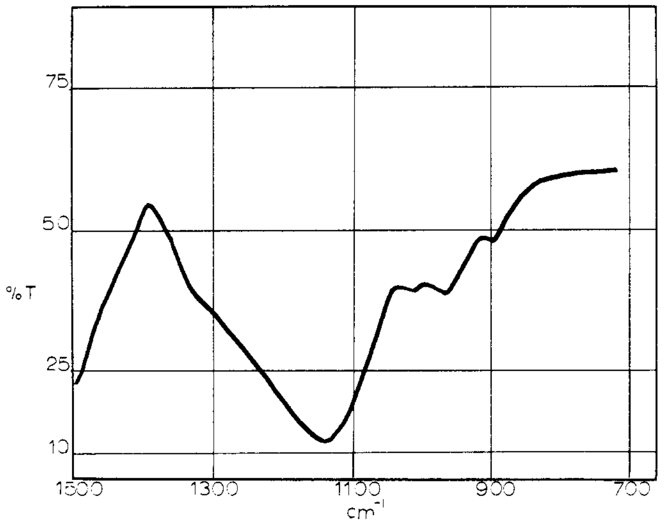

Figure 1. Infrared spectrum of ferripolyphosphate

Empirical formula: $Fe(OH)_{0.5}(PO_3)_{2.5} \cdot 5H_2O$

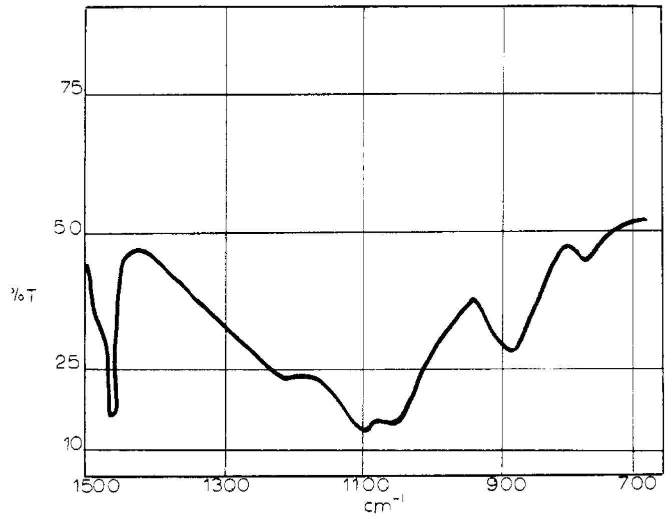

Figure 2. Infrared spectrum of ferripolyphosphate

Empirical formula: $Fe(OH)_{0.5}(PO_3)_{2.5} \cdot 5H_2O \cdot 4NH_3$

marize the effects of various drying treatments on these qualities of the ferripolyphosphate gels toward ammonia gas. The gels were prepared and desiccated with dioxane before air drying. They were not oven dried unless stated.

The volume of ammonia gas measured as being adsorbed in the modified nitrometer, when converted to a weight gained basis, is compared in Table III with the milligrams of ammonia actually found on the samples by a Kjeldahl determination. Comparison is also made to the actual weight gain of the gels.

Table II suggests that water which can be removed from freshly prepared or air dried samples by desiccating with organic solvents, as dioxane; with drying agents, $CaSO_4$; or by heating, has an inhibiting effect on the adsorptive capacity of the ferripolyphosphate for ammonia. Data of Table III show that in all samples the actual experimental gain obtained by weighing the sample is less than that calculated from the volumetric method. This can be explained from the observation that steam forms in the tube. The total water loss is less in the case of freshly prepared and air dried samples, since a reaction also occurs during the adsorption causing the adsorbent to become a sticky, red mass. For gels which have been cured by partial dehydration, the water is lost without loss of shape by the gel. The good agreement between the amount of ammonia calculated from the volumetric method and from the Kjeldahl determination in sample 5, and especially in sample 6, shows that aging is an important factor which must be considered in curing these gels for ammonia adsorption.

Table IV lists the analysis of the ferripolyphosphate before and after $NH_3$ adsorption. The infrared spectra of these samples are shown in Figures 1 and 2. The molar proportions suggest some replacement of loosely bound water molecules by ammonia molecules, but much more ammonia is present than can be accounted for by replacement alone. The infrared spectrum obtained after ammonia adsorption shows a well-defined peak between 1490 and 1450 cm.$^{-1}$, the range associated with the ammonium ion (*3*). This spectral range has been proposed as the range where one can detect the type of acidity occurring at active sites on particle surfaces (*1*). The spectral curve on Figure 2, with its band characteristic of the ammonium ion, suggests that the active sites on the gel are acting as a Lewis acid when a Lewis base is adsorbed.

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