The Adsorption of Inorganic Material
by
Precipitated Aluminum Silicate.

A thesis presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemistry.

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June 10, 1932.

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The Adsorption of Inorganic Material by Precipitated Aluminum Silcate.

Historical.

The gelatinous character of precipitated aluminum silicates suggested their possible use as adsorbents. A survey of the literature reveals many studies of the adsorption of organic material by the natural clays such as Japanese acid clay, Fuller's earth, Florida earth and kaolin. These concern special studies of these clays taken from various deposits. Many of them deal with applications of the clays to decolorizing the products of the petroleum industry.

N.A.Held[1] studied the adsorption of the chlorides of aluminum and thorium by five different Russian clays. He found that the chloridesion is adsorbed in negligible quantities, while the aluminum and thorium are adsorbed in different proportions (1 to 10 times). The cations Ca^{++} and Mg^{++} substitute Al^{+++} and Th^{++++} in the solution; i.e. reciprocal or substitution adsorption took place.

No study of adsorption by precipitated aluminum silicate could be found in the literature.

Apparatus.

A quinhydrone electrode was used in the latter part of the work, to measure the hydrogen ion concentration of the aluminum silicate suspensions. Any other apparatus used was that ordinarily in volumetric or gravimetric analysis.

Results.

The first study was arbitrarily chosen to be the adsorption of chloride ion from a sodium chloride solution. Determination of the chloride was made by titration with $AgNO_3$, with K_2CrO_4 as indicator. Due to the interference of soluble silicates in this titration, the aluminum silicate was prepared first, and added to the chloride solution in the form of a suspension. Although the titration method used is not accurate enough for the best work, it served to indicate the extent of adsorption, before any more elaborate apparatus was to be set up.

The aluminum silicate was prepared by adding an excess of $Al(NO_3)_3$ to a solution of sodium silicate, considering the reaction to be simply a replacement of Na by Al, in equivalent amount. The precipitate was washed until the filtrate gave no test for Al.

There was some doubt about the reaction taking place as one of simple replacement of one ion by another, due to the complex formation of silicates generally, but in this work it was assumed that a washed precipitate excluded consideration of this factor.

The sodium chloride solution used was one tenth normal. Approximate twentieth normal $AgNO_3$ was used for titration. The first trials were made by adding 50.cc. of aluminum silicate suspension, containing approximatly 2.0 grams of solid, to 20.00 cc. of NaCl solution. Other trials were run, by using 50.00 cc. of each, filtering and titrating a 40.00 cc. portion of the filtrate. The NaCl solution was measured out by a burette and the silicate suspension by a pipette. In each case the NaCl and $AgNO_3$ solutions were checked against each other the same day that the trials were run.

The titrations of the adsorptive mixtures prepared, ran higher in each case than the titration for an equivalent volume of the original NaCl solution. Analysis of the filtrate from these mixtures showed the presence of silica in the samples.

The aluminum silicate was washed more to remove the silica found. Some qualitative tests were next run using $KMnO_4$, to see if the permanganate ion were adsorbed in sufficient quantity to warrant its study quantitatively. The $KMnO_4$ solution used contained 0.316 grams per liter. Using this as a mother solution others were made from it by dilution to sucesssive halves until the most dilute was 1/32 that of the original concentration. 100.00 cc. portions of the aluminum silicate suspension were filtered and then 25.00 cc. portions of the various permanganate solutions were filtered through this precipitate. Comparison of the filtrates with the originals showed, that in each case, some change had taken place. The depth of color in each case appeared to be less than half the original. This was ascertained by comparison with the solution of the next lower concemtration. In the case of the most dilute solution, the permanganate color disappeared nearly completely.

An attempt to determine this loss quantitatively was the next step. The sodium silicate from which the adsorbent was the "E" brand of the Philadelphia Quartz Company. Heretofore, the silicates were of an undetermined composition. This silicate showed upon analysis of a solution of it, a Na_2O/SiO_2 ratio of 1/3.25 by weight. A filtered solution analyzed gave a ratio of 1/3.05 by weight. It was assumed, as before, that simple replacement of Na by Al, took place, although no proof of this was found.

Due to the possible effect of age upon the action of the adsorptive power of the aluminum silicate, and the lack of interference of small amounts of soluble silicates in the titration of the permanganate, the method adopted was that of precipitating the aluminum silicate in the permanganate solution. The permanganate, however, could not be titrated in the presence of the aluminum silicate because the acidity necessary for the titration prevented the silicate from forming.

To 25.00cc. of 0.001 M $KMnO_4$, 25.00 cc. each of equivalent solutions of the sodium silicate and $Al(NO_3)_3$ were added. The mixture was filtered and the permanganate titrated by 0.01 M $Na_2S_2O_3$, using KI as an intermediate reagent. The titrations titrations made upon the original $KMnO_4$ solution checked upon any one day, but varied from day to day. Hence the $KMnO_4$ and the $Na_2S_2O_3$ solutions were checked against each other, each time trials were made. The titrations were 5.25 cc. average, for 25.00 cc. of the filtrate from the aluminum silicate, and 12.10 cc. for the same amount of the original. Reduction of the permanganate seemed to take place in each trial.

Upon the suggestion of Bancroft[2] ,the study was taken up along a different line. $Al(OH)_3$ and silicic acid were tried as adsorbents for acid and basic dyes,in an attempt to determine whether it would be advisable to study an aluminum rich silicate or one that was rich in silica;also whether the positive or negative ion would prove more friutful. Along with silicic acid,and $Al(OH)_3$, Al_2O_3 and SiO_2,were also tried as suggested.

The dyes used are those given in the data.At first the various adsorbents were prepared as approximately equivalent suspensions,and added as such to dilute solutions of the dyes. These mixtures were filtered and the color compared with the original dye solutions,diluted to the same volume.In filtering, the filter paper adsorbed a great deal of dye.

Other qualitative tests were run with the same dyes but without filtering,The adsorbents were allowed to settle and then the extent of adsorption was judged from the depth of color which the settled adsorbent material had acquired.In nearly all cases,the $Al(OH)_3$ adsorbed the most material,and the silicic acid the second most.As is shown in the data,the Al_2O_3 and SiO_2 adsorbed so little,it could not be detected in this way.

Similar trials using colored positive ions,instead of dyes, showed that adsorption of them was not extensive and took place only in the case of silicic acid. The ions used were from cupric nitrate, cobalt nitrate, ferric nitrate and nickel nitrate. The silicic acid aquired only a slight color in each case.

A series of aluminum silicates, ranging from those aluminum rich to those silica rich, were prepared by the same procedure as before. These were used as suspensions and added to solutions of colored positive ions, as was previously done with the other adsorbents. The order of adsorbing power was judged as before by the depth of color acquired by the adsorbent after settling. The silicates acquired color in the case of the ferric ion, but not in the case of the cobalt, nickel or copper, except that the "C" silicate acquired a very faint cobalt ion color after several days. The ions of copper, cobalt and nickel are comparatively weak colored, and hence would not color the silicate a great deal anyway, but very dilute solutions of them did not become colorless upon standing.

The possible effect of hydrolysis in the case of the ferric ion made it advisable to check the hydrogen ion concentration against the observed coloring of the adsorbents, This showed that the silicate suspensions were not neutral. The p_H values given in the data show correlation to the observed coloring.

Discussion of Results.

The data obtained for the adsorption of the chloride ion shows that for precipitated aluminum silicate, this is negligible. The results of this are therefore in accord with the work of

N.A.Held, already referred to. Thus precipitated silicate is not any better for the purpose than the natural clays which he used.

The finding of silica in the filtrates from the chloride adsorption samples is in accord with the work of Vail[3]; this work was found too late to be of help in the work reported here. Vail noted that the reaction between a soluble silicate and a metallic salt, is not the ordinary one written for the precipitation reactions generally. The variation of either the silicate or the metallic salt solution does not produce corresponding excess amounts in the filtrate. He says that Al and silica are always found in the filtrate, and that the precipitate always contains sodium compounds. The products formed vary with the temperature also.

In view of the above, the assumption we had made in regard to the composition of the aluminum silicate is wrong, although probably the relative positions which we gave them as to whether they were at the aluminum rich end of the series or at the silica rich end is still correct.

The results with $KMnO_4$ cannot be relied upon as being due to adsorption. In nearly every case, the change of color from pink to brown indicated some other change. Permanganate is unsuited for the study unless some other method can be devised for its determination.

If we are to value Bancroft's suggestion, the greater adsorptive power of the $Al(OH)_3$ over that of the silicic acid toward both the acid and basic dyes would indicate that an alumina rich silicate would be the better adsorber for either the positive or negative ion. But since the aluminum silicates might be looked upon as combinations of oxides of aluminum and silicon, the results of the tests with these must be taken into account also. These tests would seem to indicate neither component has strong adsorptive power, and that neither the positive nor the negative ion would be adsorbed to any extent by pure aluminum silicate.

The same tests, using electrolytes instead of dyes, would indicate that a silica rich precipitate would adsorb the positive ions better since the silicic acid adsorbed some of them while the $Al(OH)_3$ did not. The apparent non-adsorption of electrolytes by both the Al_2O_3 and the SiO_2 would seem to confirm the tests made with them on dyes.

The qualitative tests on the colored positve ions, using the series of aluminum silicates as stated seems to support the conclusion that they do not generally adsorb these ions. This is in accord with the tests run using the Al_2O_3 and SiO_2, as adsorbents. The exceptional case of ferric ion where color was acquired by the silicates would seem to indicate that adsorption took place better in an acid medium than one nearly neutral or basic, since there was a correlation between the degree of adsorption observed and acidity. This conclusion holds only of course, provided it was adsorption and not hydrolysis that took place. That some hydrolysis of the ferric ion took place, with increase of time is probably true. However, with the exception of the adsorption of the dyes by the $Al(OH)_3$, it always took several hours before any color was acquired by any of the adsorbents, where such color change took place.

In view of this time factor, it seems probable that any adsorption which might occur is not simply a concentration upon the surface, but is more likely a fixation, or chemical combination. The phenomena borders on a chemical reaction, therefore. If we assume this to be true, then those aluminum silicates having residual valences at the surface, or those where there is a possibility of replacement, would probably adsorb the most material. Since the ferric ion was apparently adsorbed more strongly in an acid medium than from a neutral or basic one, it might be concluded that the acid medium has the effect of opening up more of these residual bonds.

Therefore, it seems evident that adsorption may or may not take place depending upon the structure of the silicate and the medium surrounding it. While results cannot be looked forward to with any great certainty, it appears that a study of the precipitation of aluminum silicate under controlled conditions which would give a more uniform product, and the subsequent use of these as adsorbents in media of varying p_H

might lead to the determination of the best conditions and composition for adsorption.

Summary.

The fact that the aluminum silicates studied did not adsorb inorganic material to any great extent is counterbalanced by the fact that the various natural clays are used extenxively in adsorbing organic matter.Also the fact that different clays have different adsorbing powers indicates the effect of structure on this adsorption.Also the indeterminateness of aluminum silicate prepared under conditions not rigidly controlled,suggests that methods of preparation should be studied first;and that after reproducible materials can be prepared ,the effect of composition and of the medium upon adsorption can be ascertained with greater certainty.

Bibliography.

1-Adsorption of Chlorides of Al and Th by clays and kaolins.
N.A.Held--J.of Russ.Phy.Chem.Soc.,62,1553-70(1930).
2-Bancroft,W.D.--personal conference.
3-Vail-Soluble Silicates-American Chemical Soc.Monograph.

Data.

Adsorption of Cl^- from NaCl solution:

Blank on NaCl solution 40.20 c.c. $\left\{\begin{matrix}40.20\text{c.c.}\\40.20\end{matrix}\right\}$ $AgNO_3$

Titration of same volume of NaCl solution after adsorption by aluminum silicate was 41.20c.c. $\left\{\begin{matrix}41.10\\41.30\\41.25\end{matrix}\right.$

Silica, SiO_2 found in same voume as above, 0.0050 grams.

Qualitative tests on $KMnO_4$

Solution, 0.3160 grams $KMnO_4$ per liter.

$KMnO_4$ filtered through aluminum silicate.

Concentration	Color change
full strength	marked change
1/2 "	lighter color
1/4 "	" "
1/8 "	" "
1/16 "	" "
1/32 "	" ,nearly colorless

In each case, the concentration of the color fell below that of the next lower diluted solution.

Titrations of $KMnO_4$ adsorption:

Blank on 0.001 M $KMnO_4$ by 0.01 M $Na_2S_2O_3$.
25.00 c.c $KMnO_4$ equals 12.10 c.c. $\left\{\begin{matrix}12.10\text{c.c.}\\12.10\\12.10\end{matrix}\right\}$ $Na_2S_2O_3$

Reagents added as follows:

25.00 c.c. $KMnO_4$

25.00 c.c. "E" brand sodium silicate, 0.7238 normal

25.00 c.c. $Al(NO_3)_3$ solution " "

20.00 c.c of the filtrate titrated: 1.50 c.c. $Na_2S_2O_3$
1.25
1.45
1.40
av. 1.40 c.c.

Therefore, 25.00 of the original solution becomes equivalent to 5.25 c.c. $Na_2S_2O_3$.

In each case, a brown color developed, as when the $KMnO_4$ was reduced at the filter paper. This color developed somewhat before the filtering also.

Qualitative tests using dyes, with adsorbents:
(1) $Al(OH)_3$; (2) Al_2O_3; (3) Silicic acid; (4) SiO_2

Basic dyes	Order of Adsorptive power
Nigrisine 128	1-3-2-4
Safranine	3-4-2-1
Nigrisine 2011	1-3-2-4
Crysoidine Y extra	3-2-1-4
Acid dyes	
Azo rubine	3-1-4-2
Buffalo fast violet	1-3-2-4
Wool yellow	3-1-2-4
Crystal orange	3-1-2-4
Metanil yellow(1955)	1-3-2-4
Induline(11372)	1-4-3-2
Azo bordeaux	1-3-2-4
Wool red(40 F)	1-3-2-4
Electrolytes	
$Cu(NO_3)_2$	3-1-2-4
$Co(NO_3)_2$	3-1-2-4
$Fe(NO_3)_3$	3-1-2-4
$Ni(NO_3)_2$	3-1-2-4

Qualitative tests using aluminum silicates made from C, E, BW, U, K and S, brands of sodium silicate:

Electrolytes	Order of adsorptive power
$Fe(NO_3)_3$	C, E, BW, U, K, S
$Cu(NO_3)_2$	apparently none by any.
$Co(NO_3)_2$	C, apparently none by the rest.
$Ni(NO_3)_2$	apparently none by any.

Hydrogen ion concentration of suspensions used in the qualitative tests with the series of silicates(quinhydrone electrode).

Silicate	Reading,mv.	p_H
C	-206	4.3
BW	-160	5.1
S	+126	5.7
K	+100	10.0
E	-220	4.0
U	-188	4.5