Alteration of the properties of bentonite by reaction with amines.

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Introduction.

THE affinity between certain organic compounds and clays has been known for many years. Lloyd[1] reported the adsorptive capacity of fuller's earth for alkaloids in 1916 without theorizing extensively about the mechanism. Smith[2] reacted organic bases and their salts with bentonite and presented evidence that the reaction was one of base-exchange or metathesis, while Hauser[3] has discovered that certain organic compounds of bentonite have the property of swelling and dispersing in organic liquids. This paper reports observations on the rather striking conversion of bentonite from the hydrophilic to the organophilic condition and proposes a mechanism to explain the observed phenomena.

Materials and methods.

The clay used in this work was a highly swelling sodium-bentonite from the National Lead Company property at Clay Spur, Wyoming. Thermal and petrographic analyses along with X-ray diffraction indicated the clay fraction of this material to consist essentially of the clay mineral montmorillonite. Base-exchange capacity of the purified dried clay mineral was found to be 100 me./100 g. as determined by the ammonium acetate method.[4] Sodium ion comprised approximately 86 % of the exchangeable bases.

In the preparation of the organic complexes the bentonite was

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[1] J. U. Lloyd, Discovery of the alkaloidal affinities of hydrous aluminum silicate. Journ. Amer. Pharm. Assoc., 1916, vol. 5, pp. 381–390, 490–495.

[2] C. R. Smith, Base exchange reactions of bentonite and salts of organic bases. Journ. Amer. Chem. Soc., 1934, vol. 56, pp. 1561–1563.

[3] E. A. Hauser, Private communication.

[4] R. P. Graham and J. D. Sullivan, Critical study of methods of determining exchangeable bases in clays. Journ. Amer. Ceram. Soc., 1938, vol. 21, pp. 176–183.

dispersed at about 2 % concentration in water, the dispersion set aside to permit sedimentation of non-clay impurities, and the supernatant liquid then decanted. An aqueous solution of an organic ammonium salt was then added to the clay dispersion, ordinarily in such quantity as to provide 100 milliequivalents of organic cation per 100 grams of clay. The flocculent precipitate was filtered, washed twice by repulping, dried at about 65° C., and pulverized.

Evaluation of the organophilic character of a complex so prepared was carried out by the addition of a 2-gram sample of the powder to an organic liquid contained in a graduated cylinder. After 24 hours, the volume of the swollen solids in the cylinder was recorded. Solvation took place very slowly in many liquids, and it was found necessary to add the samples in small increments, allowing each portion to solvate and sink before adding subsequent portions.

Results and discussion.

Dodecyl- and octadecylammonium bentonite complexes were prepared for which the ratio of organic salt added to clay was varied between wide limits. It was noted that filtration characteristics were best in each case when the ratio of amine to clay was in the range of 100–150 milliequivalents per 100 grams. Retention of amine, as determined by Kjeldahl analysis for nitrogen, indicated practically complete retention of the dodecylamine up to 100 me./100 g. and relatively poor retention with further additions; retention of octadecylamine decreased continuously but gradually as indicated in fig. 1. These findings parallel Grim's observation that the larger aliphatic ammonium compounds are progressively more readily adsorbed, as the size of the compound increases, after saturation of the base-exchange capacity of the clay.[1]

The viscosity of the octadecylammonium bentonite slurry, as measured with a Stormer viscosimeter at 600 r.p.m., was found to reach a maximum near the region of complete cation exchange, corresponding to the condition of maximum flocculation of the micelles, as plotted in fig. 2. This observation, along with filtration behaviour mentioned in the previous paragraph, suggests a minimum in hydrophilic characteristics of these complexes at approximately the point of complete base saturation of the exchange capacity with the organic cations.

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[1] R. E. Grim, W. H. Allaway, and F. L. Cuthbert, Reactions of different clay minerals with some organic cations. Journ. Amer. Ceram. Soc., 1947, vol. 30, pp. 137–142.

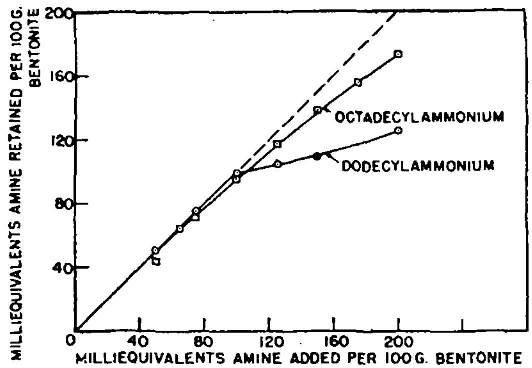

Fig. 1. Retention of organic cations by bentonite.

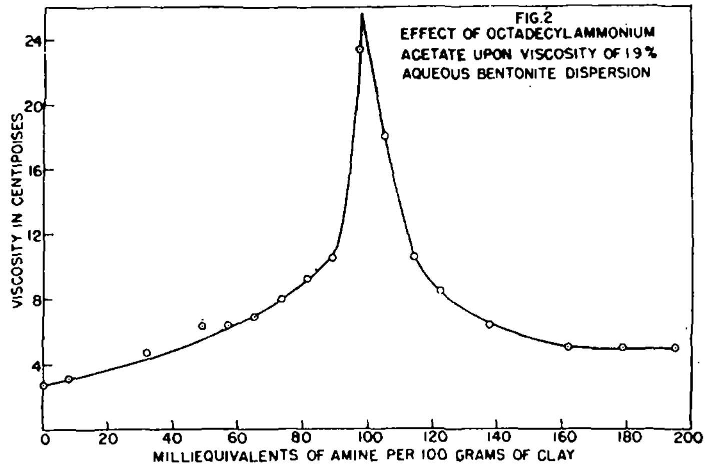

Fig. 2. Effect of octadecylammonium acetate upon viscosity of 1·9 % aqueous bentonite dispersion.

Differential thermal curves[1, 2] obtained for the untreated bentonite and for the butyl-, dodecyl- and octadecylammonium complexes after exposure to an atmosphere of 75 % relative humidity for four days point to a progressive decrease in the ability of the bentonite to adsorb moisture

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[1] J. Orcel and S. Caillère, L'Analyse thermique différentielle des argiles à montmorillonite (bentonites). Compt. Rend. Acad. Sci. Paris, 1933, vol. 197, pp. 774–777. [M.A. 6–135.]

[2] R. E. Grim and W. F. Bradley, Investigation of the effect of heat on the clay minerals illite and montmorillonite. Journ. Amer. Ceram. Soc., 1940, vol. 23, pp. 242–248. [M.A. 8–295.]

as the size of the aliphatic chain increases. This may be readily noted in fig. 3 as a diminution in size of the characteristic endothermic peak for adsorbed water with an increase in size of the organic cation. Gieseking[1] and Hendricks[2] present a picture with which this is entirely in accord. According to them the organic molecules attached to montmorillonite through base-exchange tend to be attracted more or less in their entirety on to the surface of the mineral plates, the non-cationic portion being held by adsorptive forces. Larger molecules would obviously, therefore, reduce the water-holding capacity of the clay surface.

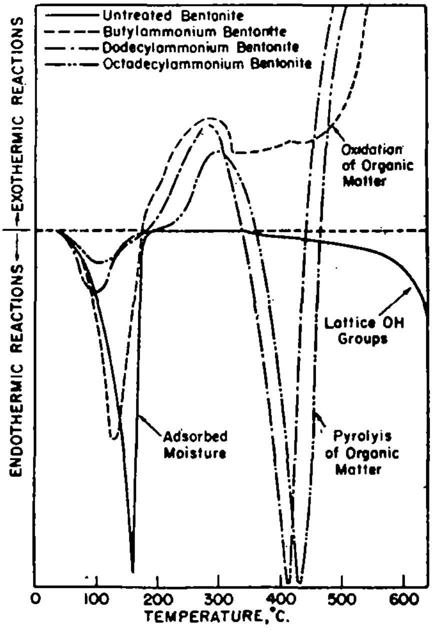

FIG. 3. Differential thermal curves.

Following the series of homologous normal primary aliphatic amines, bentonite complexes of increasingly hydrophobic character were prepared, starting with propyl- and concluding with octadecylamine. Basal-plane spacings were determined for these materials from traces obtained with a Geiger counter X-ray spectrometer. Calculating the average clay surface area per base-exchange position as 165 Å.^{2} for a clay with an exchange capacity of 100 me./100 g., the basal-plane spacings have been plotted in fig. 4 as a function of amine chain length. The stepwise separation of the flakes in increments of 4 Å., the van der Waals's thickness of a methyl group, indicates that the chains lie flat along the clay flake surfaces with the planes of the zigzag chains parallel with the planes of the mineral. On

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[1] J. E. Gieseking, The mechanism of cation exchange in the montmorillonite-beidellite-nontronite type of clay minerals. Soil Sci., 1939, vol. 47, pp. 1–13. [M.A. 8–81.]

[2] S. B. Hendricks, Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals's forces. Journ Physical Chem., 1941, vol. 45, pp. 65–81. [M.A. 8–295.]

this basis the areas covered by the amine chains have been computed from atomic dimensions[1] and included on the same graph (fig. 4). Observations appear to correlate well with theory when it is postulated that, in the case where the organic chains occupy no more than half of the available area, the organic molecules on the top surface of one lamina may fit into the gaps between those on the bottom surface of the lamina directly above it, so that the resulting separation of the two laminae is only the thickness of one hydrocarbon chain, or 4 Å. Where the chains are longer and occupy more than 50 % of the surface area, it is obvious that adjacent flakes will be unable to approach more closely than the 8 Å. thickness of two hydrocarbon chains.

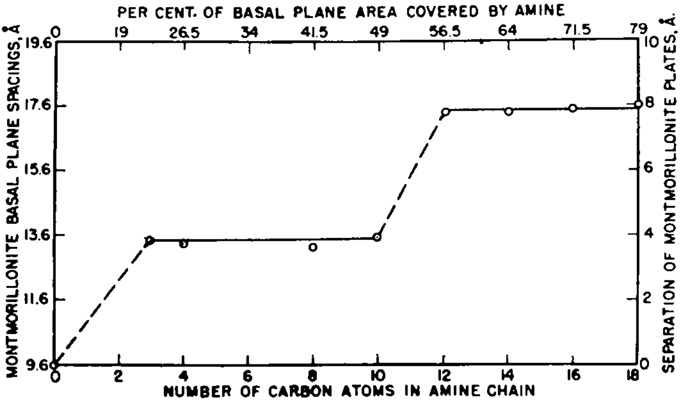

FIG. 4. Effect of amine chain length on montmorillonite basal-plane spacings.

The swelling of these various complexes in nitrobenzene and in a mixture of 90 % toluene and 10 % methanol, as plotted in fig. 5, is practically negligible until a carbon chain length of 10 atoms is reached. This coincides with the point at which 50 % coverage of the clay mineral surfaces occurs and also with the qualitative observation of thorough flocculation and rapid filtration of the aqueous amine-bentonite complex. For optimum swelling a chain length of 12 or more carbon atoms and a surface coating of more than 50 % appear to be necessary.

Choosing the dodecylammonium bentonite complex as typical of the highly swelling materials, gel volumes were determined in various single organic liquids.

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[1] L. C. Pauling, The nature of the chemical bond and the structure of molecules and crystals. Cornell Univ. Press, 1940.

Qualitative observation indicated that the most effective liquids were those which combined highly polar with highly organic characteristics, such as nitrobenzene, ethyl ether, diethyl ketone, and the like. This

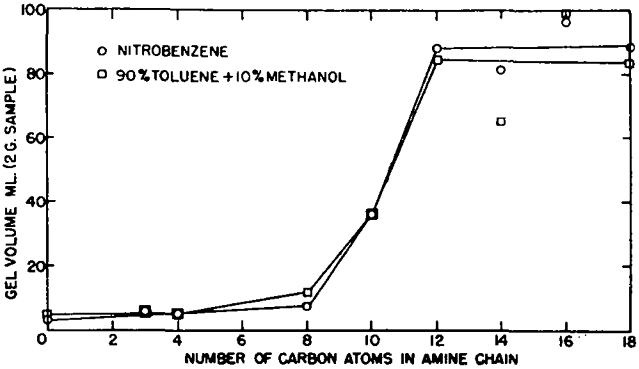

FIG. 5. Effect of amine chain length on swelling of organic ammonium bentonites in organic liquids.

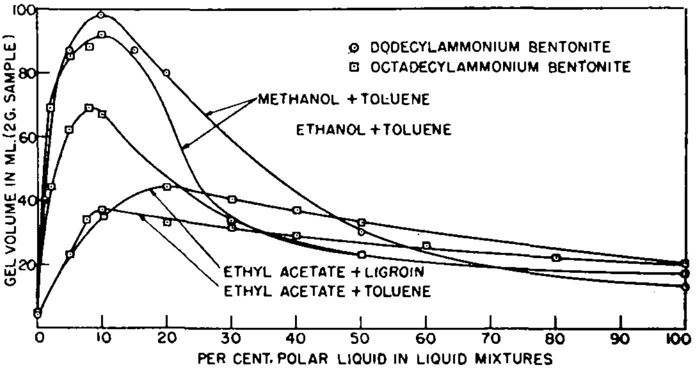

FIG. 6. Swelling of amine bentonites in binary liquid mixtures.

observation is borne out by the effect of binary liquid systems comprising a non-polar organic type of component in mixture with a highly polar liquid which may be of much less organic character. For example, dodecylammonium bentonite, which swells only slightly in toluene or in methanol, solvates very markedly in a mixture of 10 % methanol and 90 % toluene (fig. 6). Similarly, octadecylammonium bentonite swells to large volumes in mixtures of ethyl acetate with toluene or with ligroin.

The swelling of dodecyl- and octadecylammonium bentonites was determined in nitrobenzene as a function of the ratio of amine to clay in the complex (fig. 7). In correlation with previous observations of hydrophilic minima in the region of complete base-exchange, there was observed a maximum of swelling in organic liquids in the same region for both complexes. The extent of the swelling of these materials in nitrobenzene is surprising in consideration of the fact that the untreated clay swells to only about 30 ml. in water by the same test method.

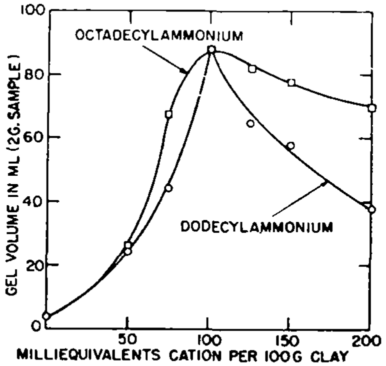

FIG. 7. Effect of varying ratio of cation to bentonite upon gel volume in nitrobenzene.

In elaborating upon the mechanism of solvation in organic liquids reference to figs. 6 and 7 should be helpful. Following the curves in fig. 7 the steep slopes of the left-hand portions of the curves indicate that satisfaction of the base-exchange capacity of the clay is essential for optimum solvation of the complex in nitrobenzene. This is probably of importance in that in an organic liquid system of this type it is desirable to mask completely or eliminate the ionic nature of the original clay by converting the sodium salt to its corresponding organic ammonium salt. The fact that further addition of organic ammonium salt beyond this point brings about a diminution in swelling may be related to a saturation of the residual adsorptive capacity of the clay by such excess reagent, thereby reducing the attractive forces available for the solvating liquid.

The part played by adsorptive forces seems well illustrated in fig. 6 where the left-hand slopes of the curves are very steep, i.e. small increments of polar liquid are extremely effective in promoting solvation of the bentonite complex. It is postulated that in a binary liquid mixture of this sort, the polar component is adsorbed on to the uncoated portion of the clay flakes. This action should tend not only to effect a further separation of the plates, making the coated surfaces more readily available for solvation, but should also completely coat the surfaces with organic matter. The completely coated flakes are therefore rendered more compatible with the surrounding liquid phase. In somewhat different terms it is hypothesized that an association complex is formed between organic ammonium bentonite and polar liquid molecules and that this complex is then solvated by the non-polar constituent of the liquid system. Excess polar liquid beyond that required to form the association complex merely tends to dilute the non-polar component, and the degree of swelling diminishes. The above picture may be carried over to single liquid systems in which the degree of swelling may depend upon the ability of the liquid to form an adsorption or association complex and subsequently upon the compatibility of the resulting complex with the liquid, keeping in mind that the character of the complex will be influenced to an appreciable extent by the long alkyl amine chains. Thus glycerol may be strongly adsorbed, but the resulting complex could not be expected to be highly compatible with glycerol; whereas, nitrobenzene should have a strong affinity for the amine bentonite salt by reason of the nitro group and should further be quite compatible with all portions of the surface coating. Hydrocarbons alone, however, are probably only weakly adsorbed and not particularly compatible with the semi-polar complex.

Summary.—Amine-bentonite complexes have been prepared and a study made of alteration of the affinities of the bentonite in connexion with various liquid systems. Several techniques have been employed in observing the change in the clay from its naturally occurring condition to one in which it is compatible with organic liquids. A mechanism is proposed to account for the pronounced modification of characteristics.