

NEW AMINE REAGENTS FOR X-RAY DETERMINATION OF EXPANDABLE CLAYS IN DRY SAMPLES*

by

R. W. REX and W. R. BAUER

California Research Corporation, La Habra, California

ABSTRACT

QUANTITATIVE X-ray diffraction analysis of minerals can most readily be performed on dry powdered samples. Current methods for determination of expandable clays require either wet oriented samples treated with glycerine or glycol or dry, randomly oriented samples treated with amines. Trimethylamine has been used to expand the montmorillonite structure to a 13.3 Å basal spacing. Unfortunately, this spacing is subject to considerable peak interferences.

We therefore undertook a review of amine-montmorillonite complexes for more suitable reagents. The formate and acetate salts of tri-n-hexylamine and of dimethylbenzylamine meet our requirements. The peak positions are the same as for glycerine complexes, while the physical properties are the same as for trimethylamine.

Detailed studies of tri-n-hexylammonium ion absorption suggest single layers of ammonium ions lying parallel to the crystal basal plane, double layers in similar orientation, and a single layer with molecules on end. The most useful orientation is the latter, which occurs in the presence of an excess of the ammonium salt and gives a montmorillonite spacing 18 Å in dry powdered samples.

Linear calibration curves with a standard deviation of about 5 per cent of the amount measured can be prepared using the conventional internal standard techniques. Minimum detectable amount of montmorillonite with rate-meter techniques is 0.4 per cent and 0.2 per cent with scalar techniques.

Several thousand analyses using tri-n-hexylammonium ion have demonstrated its effectiveness for expanding a wide variety of sediments.

INTRODUCTION

QUANTITATIVE X-ray diffraction analysis of minerals can most readily be performed on relatively dry, finely powdered, homogeneous samples. The details of the various analytical methods have been discussed by Klug and Alexander (1954). Clay minerals have posed a number of problems because of their variations in crystallinity and tendency to orient preferentially during the process of specimen preparation. Various techniques have proved useful to diminish preferred orientation, including the use of binders, propping

* Presented before the 12th Conference [1963] *Clay and Clay Minerals*.

agents and diluents. These additives are normally X-ray amorphous and may be organic or inorganic. Brindley and Kurtossy (1961, 1962) have shown that kaolinite can be determined quantitatively by X-ray powder techniques when suspended in random orientation in a thermoplastic material. Unfortunately, their plastic has to be warmed, which also dehydrates the clays. Consequently, expandable clays, such as montmorillonite, collapse their first-order basal spacings to about 10 Å, which interferes with that of the illite group of clays. G. Arrhenius (personal communication) has shown that trimethylammonium acetate can be used to expand montmorillonites to a 13.3 Å spacing. This 13.3 Å spacing serves to distinguish illite from montmorillonite. However, chlorite, if present, partially interferes with montmorillonite. Nevertheless, the trimethylamine method is useful in chlorite-free clays, because it has many advantages over the traditional glycerine or glycol expansion methods for quantitative analysis. Glycerine absorption, which is purely physical (Hoffmann and Brindley, 1961), is successful only as long as the relatively volatile glycerine wets the sample. Furthermore, glycerine expansion rates are variable and often slow. Trimethylamine gives immediate complex formation and yields a dry, homo-ionic expanded sample, stable with time and amenable to drying at 105°C.

EXPERIMENTAL PROCEDURES

Materials

Preparation of reagents

Reagent grade amines purchased from Distillation Products Division of Eastman Organic Chemicals were used for this study.

The reagents were prepared by acidifying the amine with a slight excess of formic (or acetic acid), i.e. by mixing amine and acid with a moderate amount of distilled water in a separatory funnel and checking the water pH. Sufficient acid had been added when the water pH dropped below 5. Four to six distilled-water rinses of the complex removed excess acid. If a large excess of acid had been added, it was neutralized with sodium bicarbonate. The final pH of the wash water should be about 6.5–7 if the reagent is to be used on samples containing carbonate minerals. A few hundred milligrams of sodium bisulfite were added to the water washes to inhibit amine oxidation. All reagents were stored over sodium bisulfite. The amine-formate salt was an oily liquid, which was filtered and diluted with 10 or 20 volumes of isopropanol or acetone for laboratory use.

Preparation of samples

Samples of montmorillonite were mixed with acetone solutions of the amine salt reagent and then dried. The dry powder was then packed into a planchet in a manner that minimized preferred orientation (Rex and Chown, 1960) and analyzed on both Norelco and General Electric diffractometers.

Occasionally some excess of acid remains in the reagent, which produces an extra X-ray diffraction peak at about 15 Å. If the montmorillonite sample is dried at 105°C, this peak disappears quickly without affecting the desired 18 Å peak.

A shoulder on the 18 Å amine-montmorillonite peak or a not very sharp peak usually indicates that insufficient amine has been added. The shoulder is thought to result from a 17.5 Å contribution of the double layer of amine chains.

Swelling mixed-layer clays show expansions equivalent to those of montmorillonite, and our tri-n-hexylamine reagents appear to be satisfactory for their identification.

RESULTS

The number of possible amines one might consider for analytical reagents is so large that attention was directed primarily toward those with a high probability of forming close-packed monolayers. We first reviewed primary amines as a function of chain length, then tertiary amines, some selected secondary amines, and then other miscellaneous amines that might have a suitable geometry, as suggested by model studies.

Primary Normal Aliphatic Amines

Samples of n-aliphatic amine acetate-montmorillonite complexes were prepared using concentrations (in terms of initial amounts added) of 1.00 meq amine per g of Wyoming montmorillonite of 0.73 meq per g cation exchange capacity. Two plateaus were found as reported by Jordan (1949) representing single and double layers of the amine molecular chains.

Further samples of n-amine acetate-montmorillonite were prepared by adding large excesses of the salt to montmorillonite. These amounts were not measured, but they ranged from about 4 meq per g to about 12 meq per g. The X-ray data are summarized in Table 1, where they may be compared with the theoretical spacings obtained by measuring molecular models. It shows that the experimental spacings correspond to an orientation of the ions vertical, or nearly vertical, to the basal planes.

TABLE 1.—NORMAL ALIPHATIC AMINE ACETATE-MONTMORILLONITE COMPLEXES (001) SPACINGS AT HIGH AMINE CONCENTRATION

No. carbon atoms in amine chain	6	7	8	10	12	14	16	18
Average measured spacings (Å)	18.4 ±0.2	20.6 ±0.4	21.8 ±0.2		27.1 ±0.6	29.1 ±0.2	31.9 ±0.6	34.5 ±0.2
Theoretical spacing for vertical orientation of the chains (from models) (Å)	18.6 ±0.3	20.0 ±0.3	21.3 ±0.3	23.7 ±0.3	26.2 ±0.3	28.8 ±0.3	31.2 ±0.3	34.0 ±0.3

The intensities of these peaks are, in general, high, although not quite so high as with the tri-*n*-amines. The half-peak widths are narrow. Although quantitative data are not listed, the trend is definitely toward lower intensities and broader peaks as the number of carbon atoms in the amine increases, at constant amine : clay ratio.

It appears that a fairly large excess of primary amine must be added to obtain an amine layer with molecules standing on end between the montmorillonite sheets. This results in a somewhat pasty sample that is inconvenient to handle. Consequently, we discontinued further work with primary amines.

Tertiary Normal Aliphatic Amines

The experiments used ammonium acetates and formates (Fig. 1). As might be expected, double layers of amine appear to form at lower concentration for the tertiary amines than for the primary amines or, for the same amine concentration, double layers form for shorter chain lengths with the tertiary amines.

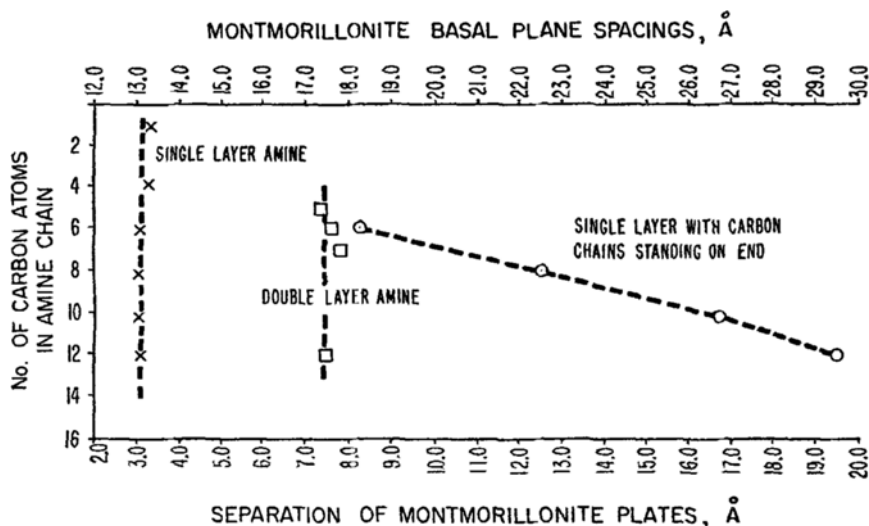


FIG. 1. Basal spacings of tri-*n*-alkyl ammonium formate-montmorillonite complexes.

The relative intensity and half-peak width measurement showed that the tri-*n*-hexylamines yielded the most intense and sharpest peaks. A study of the concentration of tri-*n*-hexylammonium acetate as a function of half-peak width (Table 2) shows a uniform peak shape once the cation exchange capacity is saturated. A detailed study of the basal spacing of montmorillonite as a function of tri-*n*-hexylammonium salt absorbed (Fig. 2) shows three plateaus. The first plateau at 13.8 Å appears to correspond to the formation of a single

TABLE 2.—HALF-PEAK WIDTH OF BASAL REFLECTION FOR TRI-N-HEXYLAMMONIUM-FORMATE CEC OF CLAY IS 0.72 MEQ/G

Amine added meq/g	Peak width at $\frac{1}{2}$ height-relative to sharpest peak obtained
0.51	1.29 ± 0.02
0.70	1.00 ± 0.02
0.79	1.02 ± 0.02
0.82	1.00 ± 0.02
1.00	1.01 ± 0.02
1.08	1.00 ± 0.02

layer of carbon chains; the second at 17.5 Å, to a double layer of chains; and the third at 18.1 Å, to a single layer with the carbon chains arranged in nearly vertical orientation. The chains are probably inclined at a high angle to the montmorillonite basal surfaces (Jordan, 1949; Weiss, 1963). Our study of the mechanism by which the tertiary amine—montmorillonite complex assumes these configurations is continuing.

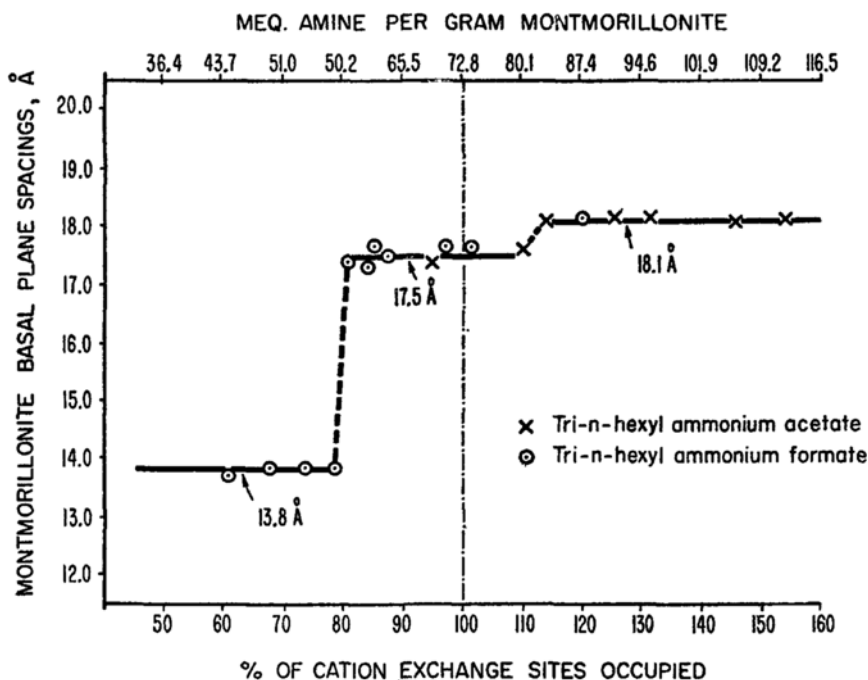


FIG. 2. Basal spacings of tri-n-hexyl ammonium acetate—and formate—montmorillonite complexes.

Secondary Normal Aliphatic Amines

Only a few of these were considered because of the scarcity of commercial sources, but di-*n*-heptylamine showed both half-peak width and peak intensity per unit weight of complex intermediate between the primary and tertiary heptylamines. Furthermore, it was harder to obtain close-packed layers of amine complex with the secondary compared to the tertiary amines. Consequently, few detailed efforts were devoted to screening this class of compounds.

Other Amines

The basal spacing of 18.1 Å which is provided by the tri-*n*-hexylammonium acetate or formate complex is very convenient for X-ray analytical purposes; therefore we restricted our review of numerous other amine-montmorillonite complexes to those providing a similar spacing. We succeeded in finding one additional compound, dimethylbenzylamine, whose formate and acetate salts proved satisfactory, providing a spacing of 18 Å. However, like the normal hexylamine acetates, it required considerably more reagent than did the tri-*n*-hexylammonium acetate to produce a monolayer-complex with the long axis of the molecule standing on end; consequently, detailed studies of this compound were not pursued further.

Influence of Various Anions

Various acids were tested for salt formation. We found satisfactory sharp peaks developed with formic and acetic acid. Propionic and heavier carboxylic acids gave broader, less sharp, peaks. Hydrochloric and sulfuric acids gave broader peaks than were obtained with formic acid.

Extensive use on natural samples suggests that formic acid gives slightly better reproducibility than acetic acid, but this was not clearly established. Both the formate and acetate salts of tri-*n*-hexylamine appear satisfactory for analytical use.

It is interesting to note that the most useful acids had anions that were both small and good aluminum complexing agents. We suspect that part of the success of this reagent is a consequence of the removal of hydroxy aluminum polymer from the montmorillonite surfaces.

Quantitative Calibration

The quantitative utility of tri-*n*-hexylammonium formate was checked in detail and that of the acetate sufficiently to verify its similarity to the formate complex.

We studied the peak height intensity of the (001) expanded montmorillonite line as a function of the amount of reagent added (Table 3). The intensity values were normalized against a kaolinite internal standard and showed a rapid increase to a plateau value beyond which no change was observed.

The physical state of the sample during this process varied from a dry free-

TABLE 3.—MONTMORILLONITE (001) INTENSITY AS A FUNCTION OF TRI-N-HEXYL AMMONIUM FORMATE CONCENTRATION

Total aliquots amine reagent added (g per g sample)	M/K	Comments
0.05	1.1	Dry powder
0.15	1.7	Dry powder
0.20	2.0	Dry powder
0.25	1.9	Dry powder
0.30	1.9	Dry powder
0.35	2.1	Dry powder
0.40	2.0	Slightly damp powder
0.45	2.1	Damp powder
0.50	2.0	Wet powder
0.55	2.1	Sticky paste

flowing powder to a pasty mass that did not affect the normalized intensity. A modest excess of amine complex can be driven off slowly at 105°C without affecting the quantitative value of the intensity. The independence of the intensity from the exact amount of amine added was checked for 10–90 per cent concentrations of montmorillonite (Table 3). For ranges of montmorillonite abundance close to the concentration of the internal standard, the standard deviation for intensity as a function of the quantity of reagent added was determined to be ± 4 per cent of the amount measured. The instrumental error was ± 2 per cent.

The measured normalized intensity, as a function of montmorillonite concentration (Fig. 3), shows a standard deviation of about 5 per cent. A

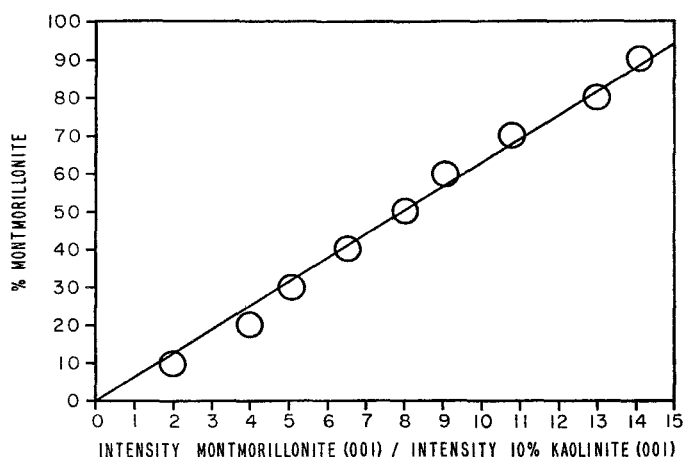


FIG. 3. Quantitative calibration for montmorillonite determination using 10 per cent kaolinite as internal standard.

minor problem in preparation of standard curves is the hygroscopicity of montmorillonite. Another possible source of error is variation among montmorillonite standards from different areas.

Maximum sensitivity for montmorillonite determination using our amine reagents varies according to the instrumentation. We can significantly measure 0.4 per cent montmorillonite using rate-meter techniques and 0.2 per cent using scalar techniques with a Norelco diffractometer, Cu $K\alpha$, 50 kV, 40 mA, 1° slits, nickel filter, and pulse height filtering of secondary iron fluorescence.

SUMMARY

We undertook a review of amine-montmorillonite complexes to search for compounds suitable for routine use as expanding agents for X-ray determination of montmorillonites and found four compounds that met our requirements. They are the formate and acetate salts of tri-*n*-hexylamine and dimethylbenzylamine. They yield expanded montmorillonite with first-order basal spacings of 18.1 Å, essentially the same as the currently used glycerine complex.

Detailed studies of tri-*n*-hexylammonium formate and acetate suggest that they are stable with time and produce a homo-ionic, nonhygroscopic clay. The complex yields an intense peak useful for quantitative analysis. Furthermore, the reagent is satisfactory for use with both oriented aggregate slides and for random packing mounts.

ACKNOWLEDGMENTS

The helpful and stimulating comments of our colleagues, Drs. C. D. McAuliffe and S. R. Silverman, assisted greatly in the preparation of this paper and are gratefully acknowledged.

REFERENCES

- BRINDLEY, G. W., and KURTOSY, S. S. (1961) Quantitative determination of kaolinite by X-ray diffraction, *Am. Mineralogist* **46**, 1205–15.
- BRINDLEY, G. W., and KURTOSY, S. S. (1962) Quantitative determination of kaolinite by X-ray diffraction, A reply to H. W. van der Marel, *Am. Mineralogist* **47**, 1213–15.
- HOFFMAN, R., and BRINDLEY, G. W. (1961) Adsorption of ethylene glycol and glycerol by montmorillonite, *Am. Mineralogist* **46**, 450–2.
- JORDAN, J. W. (1949) Organophilic bentonites. I. Swelling in organic liquids, *J. Phys. Chem.* **53**, 294–306.
- KLUG, H. P., and ALEXANDER, L. E. (1954) *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, John Wiley, New York.
- REX, R. W., and CHOWN, R. G. (1960) Planchet press and accessories for mounting X-ray powder diffraction samples, *Am. Mineralogist* **45**, 1280–2.
- WEISS, A. (1963) Mica-type layer silicates with alkylammonium ions, *Clays and Clay Minerals*, 10th Conf. [1961], pp. 191–224, Pergamon Press, New York.