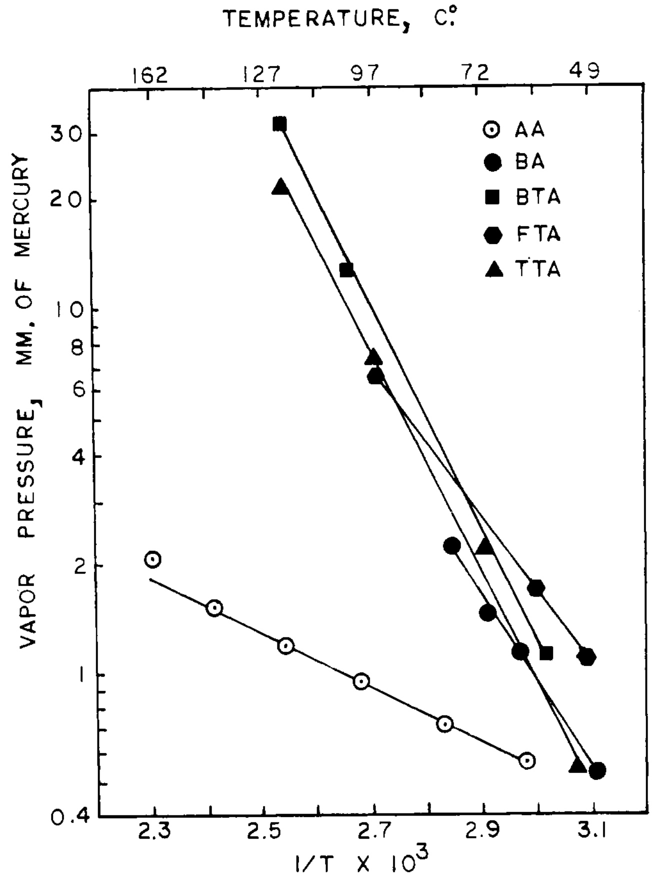

Figure 1. Vapor pressure *vs.* 1/*T* for some β-diketone chelate compounds of cobalt(III)

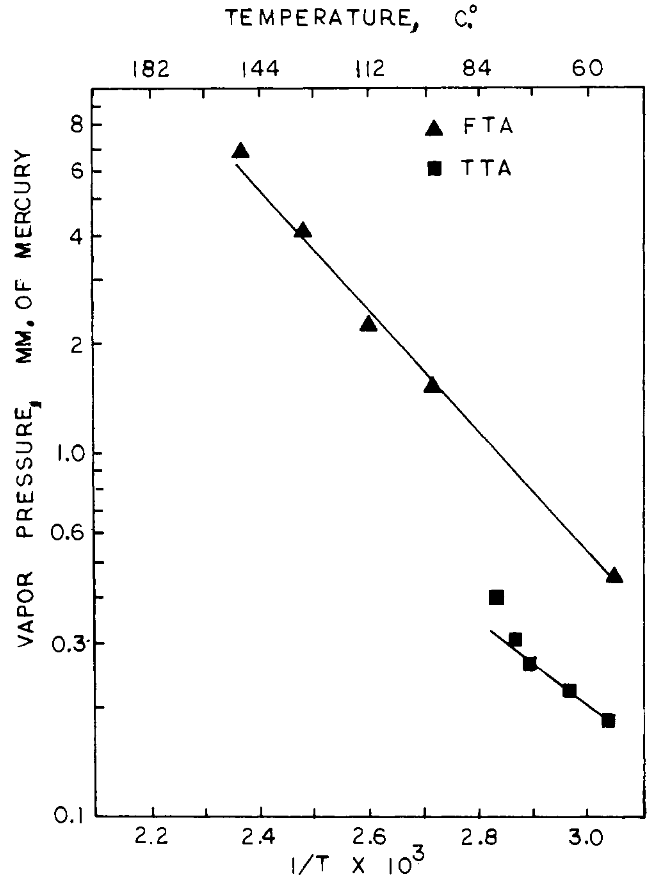

Figure 2. Vapor pressure *vs.* 1/*T* for some β-diketone chelate compounds of iron(II)

cates the matter that no logical explanation for the observed differences can be presented.

Attempts to isolate the iron(II) chelates of acetylacetone, benzoylacetone, and benzoyltrifluoroacetone were not successful, but there was ample evidence for their existence in solution. Reaction mixtures turned purple immediately upon mixing reagents, but the purple products reverted to the red iron(III) form on exposure to the atmosphere. It is well known that this type reaction can take place in solutions or solids very easily and that the more electrophilic the substituent group, the more stable is the iron(II) chelate (*2*). This is the probable explanation for the greater stability of the iron(II) FTA and TTA chelates, since the furoyl, thenoyl, and trifluoromethyl groups act as electrophilic groups.

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Sorption of *n*-Butylammonium and *n*-Dodecylammonium Acetate by Sodium Montomorillonite and Sodium Vermiculite

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A CHEMICAL or physical-chemical reaction takes place between certain organic materials and soils, clays, and resins. This reaction was attributed (*8*) to an ion exchange mechanism, wherein the organic salt ions formed complexes with the solid materials by displacing the inorganic ions originally present in the solid. Originally, it was assumed and some experimental evidence indicated (*4*) that the major portion of the exchangeable cations were located on the surface.

Later evidence (*5*) indicated that the reaction involved more than surface cation replacement by the organic salt ion because the *C*-axis spacing of montmorillonite was increased, indicating an interlayer cation reaction. This observation was substantiated by later work (*1, 4, 6, 9*) which showed that the sorption of large aliphatic ammonium ions exceeded that of the "normal" ion exchange capacity of the solid structure.

The solid materials on which these studies have been made and reported on are: bentonite (montmorillonite), vermiculite, and synthetic ion exchange resins.

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The organic compounds studied in this respect have been organic colloids, primary, secondary, and tertiary aliphatic amines, and gelatin. The amines ranged in chain length from ethylamine to tetradecylamine.

This experimental investigation was conducted for the purpose of studying the extent of reaction of *n*-butylammonium and *n*-dodecylammonium salts with montmorillonite and vermiculite (the approach to equilibrium), the retention of alkyl ammonium ions by the complexes after water washing, and the *C*-axis spacing after formation of complexes. From these data, the actual size and shape of the amine molecules and possible arrangements of the ions in the interlayer spaces could be postulated.

Characteristics of Montmorillonite and Vermiculite Structure. The unit structure of montmorillonite as proposed by Hofman, Endell, and Wilm is modified by Maegdefrau and others as described by Grim (*2*), is composed of one layer of alumina octahedra sandwiched between two layers of silica tetrahedra with oxygen atoms common to the alumina layer and either of the silica layers. Thus the silica-alumina-silica unit surfaces are composed of oxygen atoms with some hydroxyl groups around the edges. The units are stacked one above the other so that the oxygen surfaces of one unit are adjacent to the oxygen surfaces of adjacent units. The O—O bonds are weak and polar compounds enter between the units causing expansion of the structure along the *C*-axis.

Montmorillonite has the property of permitting substitution of atoms of lesser valence for aluminum atoms in the octahedra layers. This causes an electrical change unbalance amounting to −0.66 per unit cell. The deficiency is balanced by exchangeable cations between the layers or around the edges.

Montmorillonite has approximately 160 sq. A. of oxygen surface per unit charge or 80 sq. A. of surface area per one basal plane per unit charge (*3*). Vermiculite has essentially the same basic structure as has montmorillonite. The electrical unbalance is chiefly the result of substitution of Al^{+3} for Si^{+4} in the tetrahedral layers. The charge deficiency of vermiculite is −1 to −1.4 per unit cell and the total oxygen surface area per unit charge is estimated to be about 75 sq. A. and for each basal plane per unit charge, 48 sq. A. (*3*).

Cation Exchange Capacity. The cation exchange capacity is reported as milliequivalents per 100 grams of solid. This exchange capacity arises from charge deficiency between the interlayers (ca. 80%) and around the edges (ca. 20%). The exchange capacity of montmorillonite is approximately 100 meq. per 100 grams and that of vermiculite around 150 to 200 meq. per 100 grams.

The exchange capacity is commonly determined by saturating a known amount of clay with NH_4^+ ions, washing to remove mechanically adhering NH_4^+, and then treating with NaOH. The NH_3 is distilled off, absorbed, and titrated.

Materials. The amines used in this study while not of "chemically pure" grade, were considered to be of sufficient purity. The *n*-butylamine was estimated to be of 90%+ purity and the *n*-dodecylamine was stated to contain 95 to 99% of *n*-dodecylamine.

The clay minerals were a sodium-saturated Wyoming bentonite having an exchange capacity of approximately 90 meq. per 100 grams, and a Llano (Texas) high-exchange capacity Mg.-vermiculite having an exchange capacity of approximately 200 meq. per 100 grams. The Mg-vermiculite was converted to Na-vermiculite by treatment with a strong solution of NaCl.

X-ray diffraction analysis showed the montmorillonite to be Na montmorillonite and the vermiculite to be mono-water-layer Na vermiculite.

The amines were converted to *n*-butylamine acetate and *n*-dodecylamine acetate and used in approximately 1*M* concentrations. Montmorillonite was used as a slurry containing approximately 3.5 weight % of the mono-water-layer Na montmorillonite and the mono-water-layer Na vermiculite was used in dry powdered form.

Procedure. A known amount of montmorillonite slurry or vermiculite powder was placed in a centrifuge tube and a selected amount of alkylammonium salt added to get the desired alkylammonium ion to clay ratio. The mixture, diluted to approximately 33:1 weight ratio with water, was shaken vigorously at intervals over a 26-hour period. The temperature was maintained at 70° F.

At the end of the 26-hour period, the tube and contents were centrifuged and the supernatant liquid was separated from the clay complex, weighed, and transferred to a Kjeldahl flask. The clay complex was then washed, and the washings were weighed and added to the flask. The quantity of NH_3 was determined by the Kjeldahl method, and the amount of alkylammonium salt unreacted was calculated.

The butylammonium complex sample for x-ray analysis was prepared by drying a drop of slurry on a glass slide at 50° C. The dodecylammonium complex sample was dried at 50° C., ground to a powder, and used in the form of a powder pack for x-ray analysis.

DISCUSSION OF RESULTS

In calculating the amount of alkylammonium complex sorbed as a clay complex, the following observations were used as a basis.

The x-ray diffraction patterns obtained indicated that the clay was a mono-water layer modification.

According to the following equation

$$Na^+\,\text{clay} + RNH_2H^+Cl^- \rightarrow RNH_2H^+\,\text{clay} + Na^+Cl^-$$

one ammonia group may replace on Na^+. In the case where the measured absorbed quantities of amine on the clay are greater than the amount of Na^+ on the clay as measured by its exchange capacity, the excess amine was adsorbed as free RNH_2.

The average estimated per cent deviation in the butylammonium acetate data was ± 5.0% and in the dodecylammonium acetate data ± 1.0%.

Sodium Montmorillonite. Sorption data for butylamine acetate on sodium montmorillonite (Table I) indicate a relatively high sorption of the butylammonium ion (relative to the exchange capacity of clay) with exposure to amounts of ion less than the exchange capacity. Exposure of the clay to amounts of RNH_3^+ greater than the exchange capacity resulted in a maximum sorption of the amine equivalent to about 85 meq. per 100 grams of clay. This was not exceeded even with exposure to solutions containing 1250 meq. per 100 grams.

The *C*-axis spacing for montmorillonite saturated with butylammonium acetate was found by x-ray analysis to be 13.2A. The interlayer spacing is 3.8A., so that the ions must be imbedded in the lattice. The arrangement might be as shown in Figure 1.

Sorption data for dodecylamine ion on montmorillonite are shown in Table I. These show almost complete sorption of the ion at low concentrations and at high concentrations the limiting value of 190 meq. per 100 grams of clay is reached. Since the cation exchange capacity of the clay is around 100 meq. per 100 grams, there is an excess of ions sorbed. If only amine molecules are sorbed in excess of the exchange capacity, there is obviously some limitation on the sorption caused by the mechanism involved.

In the low concentration range of dodecylammonium acetate (the first four points of Table I) an abnormality is indicated. This is probably caused by contamination of the centrifuged supernatant liquid by suspended particles of clay complex. Where low concentrations—i.e., a higher proportion of solid to liquid—were encountered it was impossible to obtain solid-free liquid samples with the technique utilized. For this investigation, the saturation concentration range was of principal interest and development of techniques necessary to develop highly accurate data in the low concentration range was considered unnecessary.

Washing removed the amine sorbed in excess of that indicated by the exchange capacity. This would tend to indicate weak adsorptive forces holding the excess amine through adsorption.

The ΔC-axis spacing for the washed dodecylammonium-clay complexes with the exchange sites saturated was found to be 8.2A. by x-ray analysis.

Sodium Vermiculite. The sorption data for butylamine acetate on sodium vermiculite are shown in Table I. Data indicate that very little sorption takes place when the quantity of amine salt added is less than the exchange capacity. When the clay is exposed to quantities in excess

Table I. Sorption Data for *n*-Alkylammonium Acetates on Sodium-Clay Minerals

(In milliequivalents/100 grams of clay)

Sample Number	Amount Initially Added, $M_{A,i}$	Amount in Liquid at Equilibrium, $M_{A,L}$	Amount Retained by Clay at Equilibrium, $M_{A,Z}$	Amount Retained by Clay after Wash
		n-Butylammonium Acetate on Sodium-Montmorillonite		
1	48.1	8.2	39.9	
2	74.9	17.1	57.8	60.8
3	81.9	17.8	64.1	
4	99.2	26.8	72.4	
5	116.1	41.9	74.2	72.7
6	130.0	51.3	78.7	78.2
7	173.4	90.3	83.1	75.7
8	203.2	120.3	82.9	
9	220.0	136.4	83.6	80.3
10	312.0	226.8	85.2	
11	409.3	325.1	84.2	
12	438.1	354.7	83.4	
13	515.6	430.9	84.7	81.8
14	614.5	531.3	83.2	
15	774.4	691.1	83.3	80.0
16	872.1	791.8	79.3	81.0
17	1008.9	928.4	80.5	82.6
18	1139.1	1058.4	80.7	80.5
19	1238.4	1154.2	84.2	81.4
20	1254.7	1169.8	84.9	81.2
		Dodecylammonium Acetate		
1	20.6	5.1	15.5	
2	52.8	4.7	48.1	48.1
3	70.5	2.7	67.8	68.1
4	96.5	4.5	92.0	89.4
5	149.9	18.6	131.3	104.5
6	164.6	22.0	142.6	
7	195.3	30.1	165.2	112.6
8	235.9	58.5	177.4	
9	278.5	97.9	180.6	
10	347.6	160.8	186.8	
11	347.7	162.8	184.9	122.0
12	472.4	280.9	191.5	
13	522.2	333.1	189.1	136.0
14	597.6	409.1	188.5	
		n-Butylammonium Acetate on Sodium-Vermiculite		
1	47.0	42.6	4.4	0
2	86.1	79.4	6.7	0
3	146.2	137.5	8.7	2.1
4	196.9	182.3	14.6	2.9
5	267.7	243.4	24.3	14.3
6	424.0	375.4	48.6	36.2
7	648.5	554.4	94.1	83.3
8	868.1	740.6	127.5	115.1
9	953.6	810.3	143.3	132.2
10	1258.9	1104.9	154.0	137.0
11	1516.4	1342.9	173.5	157.1
12	1765.0	1589.0	176.0	162.7
13	2044.5	1858.1	186.4	172.1

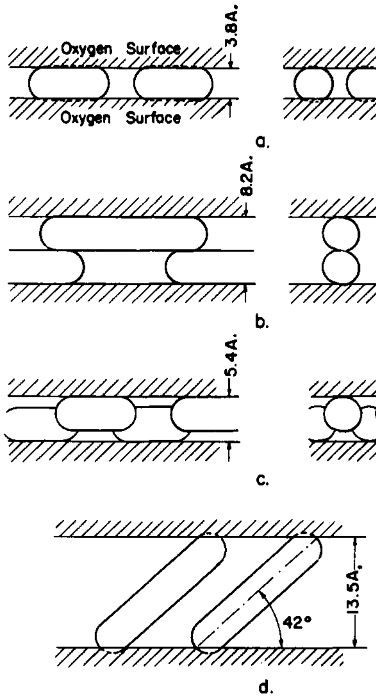

Figure 1. Speculated arrangement of interlamellar ions

a. Exchange positions of montmorillonite saturated with *n*-butylammonium ions
b. Exchange positions of montmorillonite saturated with *n*-dodecylammonium ions
c. Exchange positions of vermiculite saturated with *n*-butylammonium ions
d. Exchange positions of vermiculite saturated with *n*-dodecylammonium ions

Table II. C-Axis Spacings for Butylammonium Acetate on Sodium-Vermiculite

Sample No.	Amount of Amine Salt Initially Added, Meq./100 Grams	*C*-Axis Spacing, A.
	Equilibrium Clay Complexes	
1	35.4	11.8
2	85.4	11.8
3	132.0	11.8
4	184.6[a]	11.8
5	317.5	11.8
6	438.8[b]	11.8
7	540.2[b]	11.8
8	726.1	14.7
9	901.5[c]	14.7
10	1220.5	14.7
11	1612.1	14.7
12	1893.8	14.7
	Washed Clay Complexes	
1	47.0	11.8
2	86.5	11.8
3	146.2	11.8
4	196.9[a]	11.8
5	267.7	11.8
6	424.0[b]	11.8
7	648.5	14.7
8	868.1[c]	14.7
9	953.6	14.7
10	1258.9	14.7
11	1516.4	14.7
12	1765.0	14.7
13	2044.5	14.7

[a] First appearance of 14.7 A., *C*-axis spacing pattern. [b] Both patterns about equally intense. [c] Last appearance of 11.8 A., *C*-axis spacing pattern.
11.8 A. is *C*-axis spacing of Na-vermiculite.

of the exchange capacity, sorption approaches the exchange capacity of 200 meq. per 100 grams. Washing removed and sorbed material absorbed at low concentrations indicating, probably, adsorption on the surface. At higher concentrations, the structure is apparently forced apart, allowing interlamellar adsorption.

This observation is supported somewhat by x-ray analysis on the low concentration range amine-contracted clay, the intermediate, and the high concentration range. The low concentration range indicates the structure to be all sodium vermiculite, the high range indicates the structure to be saturated with amine, and intermediate which shows vermiculite either containing no amine (the Na-vermiculite structure) or completely saturated. In no case was it indicated that partial saturation of the structure was obtained.

X-ray study of the washed samples showed the ΔC-axis spacing to be 5.4 A. when saturated. From the area per unit change, 75 sq. A., and the area of the butylamine, 44 to 40 sq. A., over 50% of the area is covered. Therefore, the possibility of stacking is indicated.

Sorption data for dodecylamine are given in Table II. Vermiculite sorbs almost all of the organic ions for concentrations below 200 meq. per 100 grams. At higher concentrations, the constant value of about 300 meq. per 100 grams is reached. This is about 50% in excess of the exchange capacity compared to about 110% for montmorillonite. This is logically based upon the larger area per unit change for montmorillonite. Washing removes amine in excess of the exchange capacity indicating again the excess is held in place by much weaker forces than those for the material held by ion exchange.

X-ray diffraction studies indicated vermiculite to have a Δ C-axis spacing of 13.5 A. when the exchange sites were saturated. This would require that ions be adsorbed at some angle to the C-axis or that there was a distortion of the organic molecule.

CONCLUSIONS

Sodium montmorillonite and sodium vermiculite will sorb the butylamine molecule, butylammonium ion, or butylammonium acetate in quantities slightly less than the exchange capacity.

Both clay forms will sorb in some form the dodecylamine molecule, ion, or salt in quantities in excess of their exchange capacities.

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Molar Refraction

The Extension of the Eisenlohr-Denbigh System of Correlation to Liquid Organotin Compounds

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THE DENBIGH (*3, 24*) system of bond refractivities, based on the classical Lorenz-Lorentz equation

$$MR_L = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

has been successfully employed in the field of organotin compounds by West and Rochow (*30*) and by Vogel, Cresswell, and Leicester (*27*). The subject is treated briefly in a recent review by Gillis (*5*). Because of the demonstrated superiority of the combined Eisenlohr and Denbigh concepts in providing a useful tool for research on liquid organophosphorus compounds (*21*), the present investigation was undertaken primarily to evaluate the merits, in their application to liquid organotin compounds, of each of four systems of correlation—*viz.*, two using refractivities (atomic and bond) based on the Lorenz-Lorentz equation, and two using refraction constants (atomic and bond) based on the empirical Eisenlohr molar refraction product, $MR_E = Mn^{20}_D$ (*4*).

Table I. Calculated Parameters

Atomic Refractivities		Bond Refractivities				Atomic Refraction Constants		Bond Refraction Constants	
		Bond	West & Rochow (*30*)	Vogel, others (*27*)	Present work				
Sn	14.156	Sn-C$_{al}$	4.09 (prim.) 4.24 (sec.)	4.16	4.170	Sn	197.90	Sn-C$_{al}$	54.09
$-\overset{\mid}{\underset{\mid}{\mathrm{C}}}\mathrm{H}$	3.791	Sn-C$_{ar}$	3.54	3.78	4.548	$-\overset{\mid}{\underset{\mid}{\mathrm{C}}}\mathrm{H}$	22.00	Sn-C$_{ar}$	64.14
		Sn-Cl	8.81	8.91	8.664			Sn-Cl	100.75
		Sn-Br	12.02	12.00	11.971			Sn-Br	179.65
$-\overset{\mid}{\underset{\mid}{\mathrm{C}}}-$	2.981	Sn-I	17.95	17.92	17.407	$-\overset{\mid}{\underset{\mid}{\mathrm{C}}}-$	23.41	Sn-I	259.40
		Sn-O	3.84	3.84	2.928			Sn-O	61.81
		Sn-S			7.631			Sn-S	84.46
		Sn-Sn	10.96	10.77	10.683			Sn-Sn	114.81

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