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Intercalation of Dodecyl Sulfate into Layered Double Hydroxides

A. CLEARFIELD, M. KIEKE[1], J. KWAN[1], J. L. COLON[2] and R.-C. WANG[3]
Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

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Abstract. The intercalation of sodium dodecyl sulfate and exchange of dodecyl sulfate anion into layered double hydroxides has been examined by means of X-ray diffraction, infrared and thermogravimetric procedures. Three types of derivatives were obtained having mean interlayer spacings of ~26 Å, 36 Å and 47 Å, respectively. These interlayer distances did not correlate with the amount of organic incorporated between the layers but, as shown by computer simulations, depended upon the orientation of the chains within the interlamellar space. In several reactions both intercalation of neutral sodium dodecyl sulfate as well as exchange of the dodecyl anion took place. Attempts to remove the alkyl sulfate chains with dilute acid resulted in dissolution of the more basic metals producing non-stoichiometric layered products.

Key words. Intercalation, X-ray powder diffraction, infrared, thermogravimetric analysis, dodecyl sulfate.

1. Introduction

Layered double hydroxides constitute an interesting and extensive class of layered compounds [1]. Their general composition may be represented as $M(II)_n M(III)(OH)_{2n+2}X$, where $n = 2$–5 and X is a charge balancing anion. The layers have the $Mg(OH)_2$ structure in which the trivalent metal is isomorphously substituted [2, 3]. This substitution creates positively charged layers balanced by anions in the interlamellar space as shown in Figure 1. However, three main structure types have been identified [4]: hydrotalcite, $Mg_n Al(OH)_{2n+2}X$; pyroaurite and sjogrenite of composition $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4\,H_2O$, which have different stacking modifications. Reichle [5] has provided an extensive account of synthetic procedures for various layered double hydroxides (LDH). A variety of anions may be readily exchanged into the LDH [6–8]. Very large anionic species have recently been exchanged with the purpose of propping the layers apart [9–11]. Drezdon [9] first separated the layers by incorporating an organic acid between the layers and this facilitated the subsequent exchange of the isopolymetallate anion. A similar procedure was followed by Dimotakis and Pinnavaia [12]. However, they first heated the LDH to 500°C to convert it to the oxide form and then reconstituted the LDH in water in the presence of glycerol. In this form, the interlayer spacing exceeded 40 Å. Both the calcined LDH and the pillared derivatives show promise in catalytic applications [6, 9, 13, 14].

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[1] Undergraduate R. A. Welch Foundation Scholars.

[2] Present Address: California Institute Tech.

[3] Present Address: Shell Development Corp./Houston, TX

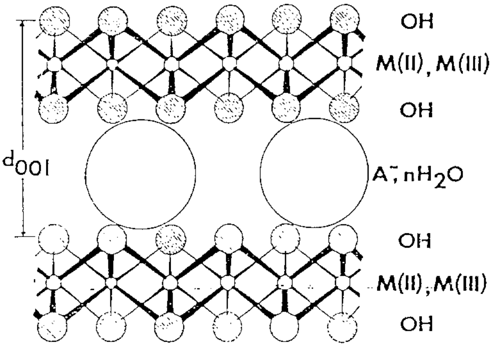


Fig. 1. Schematic drawing of the layered double hydroxide structure.

We were interested in the organic intercalates *per se*. A series of linear aliphatic dicarboxylate LDH intercalates was described by Miyata and Kimura [15]. Drezdon [9] could not duplicate these preparations but he succeeded in incorporating several sulfonic acid anions as well as the terephthalate anion. Treatment of these intercalates with dilute acids such as HCl or HNO_3 resulted in the exchange of the acid anion for the organic acid anion except for dodecyl sulfate. We therefore decided to investigate the intercalation-deintercalation reactions of dodecyl sulfate with several LDH. Some preliminary studies on this system have been reported [9, 16–18] as well as a more detailed study of sulfonic acid intercalates [19].

2. Experimental Section

2.1. PREPARATION OF LAYERED DOUBLE HYDROXIDES

Three series of layered double hydroxides were prepared; nickel aluminum hydroxy chlorides, $Ni_nAl(OH)_{2n+2}Cl$, $n = 2–5$, magnesium aluminum chlorides, $Mg_nAl(OH)_{2n+2}Cl$, $n = 2–5$ and zinc chromium chloride LDH $\sim Zn_2Cr(OH)_6Cl$. The general procedure involved adding a mixture of the metal chlorides (approximately 1M in total metal concentration) in the correct ratio, from a burette to a large beaker containing 100 mL of water and kept at 70°C. At the same time, a 2M solution of NaOH was added with vigorous stirring at a rate such as to keep the pH close to 10. After the addition was complete heating was continued for 4 to 24 h while keeping the water level constant. To this point, all the operations were carried out under nitrogen. The precipitate was then filtered off and washed with distilled, deionized water until free of Cl^-. The solid was initially air dried and then evacuated overnight or dried at 70°C. Analytical data for a number of preparations are collected in Table I.

The dedecyl sulfate anion, $CH_3(CH_2)_{11}SO_4^-$, was intercalated in two different ways. A weighed quantity of LDH in the chloride form was added to water in the ratio of 1 g per 20 mL of water. The mixture was stirred until homogeneous and a solution of sodium dodecyl sulfate (0.7M) was added while keeping the pH constant at 10. The mole ratio of sulfate to LDH varied from 0.1 to 2. Stirring was

Table I. Elemental analysis of layered double hydroxides.

Sample No.	RW-56A		RW-56D		RW-1-83		RW-1-86	
Element	% obs	% Calc[a]	% obs	% Calc[b]	% obs	% Calc[c]	% obs	% Calc[d]
Mg	25.14	25.16	19.76	19.73	—	—	—	—
Ni	—	—	—	—	34.19	34.02	44.60	44.8
Al	5.91	5.91	11.13	11.18	7.94	7.90	4.21	4.23
Cl	7.34	7.32	10.96	10.96	7.52	7.47	5.67	5.55
C	0.4	0.4	0.64	0.64	0.66	0.5	0.5	—
H	4.41	4.46	4.09	3.93	3.23	3.79	2.91	3.42
H_2O	17.2*	17.75	—	13.36	18.9	18.46	12.8	14.11

[a] Based on the formula $Mg_{4.72}Al(OH)_{11.2}Cl_{0.94}(CO_3)_{0.15}\cdot 4.5H_2O$.
[b] Based on the formula $Mg_{1.97}Al(OH)_{5.94}Cl_{0.75}(CO_3)_{0.13}\cdot 1.8H_2O$.
[c] Based on the formula $Ni_{1.98}Al(OH)_{5.96}Cl_{0.72}(CO_3)_{0.14}\cdot 3.5H_2O$.
[d] Based on the formula $Ni_{4.87}Al(OH)_{11.74}Cl\cdot 5H_2O$.
*From TGA.

continued for 4 to 24 h. Then the solid was either filtered or centrifuged off, washed three times with 200 mL portions of distilled deionized water, followed by two washings with 100 mL portions of methanol and air dried. Several variations of this general procedure, as indicated in the text, were tried.

The second method was to intercalate the dodecyl sulfate at the same time the LDH was prepared. An excess of sodium dodecyl sulfate, usually 2–3 moles per mole of LDH, was dissolved in 2N carbonate free NaOH. A second solution consisting of the two metal chlorides in the desired ratio was prepared also in carbonate free water. This solution was added rapidly to the sodium dodecyl sulfate solution with vigorous stirring and after addition was complete, the pH was adjusted to a value of 10. Stirring was continued for 4 to 24 h and the solid recovered, washed and dried as before. The entire operation up to solid recovery was carried out under nitrogen.

2.2. REAGENTS

The hydrated metal chlorides were all Fisher reagent grade and used without further purification. Sodium dodecyl sulfate was Aldrich 98% purity. NaOH (Fisher reagent grade) was freed of CO_2 by passage through an anion exchange resin in the hydroxyl form contained in a chromatographic column. Distilled deionized water was boiled before use to remove oxygen and CO_2.

2.3. INSTRUMENTAL AND ANALYTICAL

X-ray diffraction patterns were recorded with a Scintag PAD-II powder unit with CuK_α (filtered) radiation. The scan speed was usually 1°/min at 40 kV and 20 mA. In some cases the patterns were obtained by step scanning at 0.05° per step and 10 sec count time. Infrared spectra were obtained with a Bio-Rad (Digilab) FTS-40 spectrometer by the KBr disk method. Thermal analysis was carried out with a DuPont Thermal Analysis 2000 unit at heating rates of 4 to 10°/min under N_2 unless otherwise specified. Elemental analysis was carried out either by Galbraith Laboratories or internally by AA and inductively coupled plasma arc methods. Surface areas were measured by the BET N_2 sorption method on an Autosorb-6 (Quantachrome) automated gas adsorption unit. The sample was outgassed at 200 °C for 36 h prior to degassing in the sorption unit for 30 h. This degassing procedure was necessary because of the high content of water and methanol of the freshly washed sample. A 40 point isotherm in both sorption and desorption modes was recorded.

3. Results

Analyses of the LDH were carried out for the end members of the two series ($n = 2$ and 5) and found (Table I) to conform fairly well to the expected 2:1 and 5:1 ratios of divalent to trivalent metal. X-ray diffraction patterns of selected LDH are shown in Figure 2. These patterns show the first three (001) reflections and one or two others. In general it was found that the longer the aging at 70° the sharper were the X-ray reflections indicating greater degrees of crystal perfection. The products which contained some carbonate ion exhibited somewhat broader reflections than those which did not. All members of the series with $n = 2$ to 5 were prepared for the Mg–Al and Ni–Al LDH but only one compound with Zn/Cr = 2 was obtained. Interlayer spacings of representative preparations are given in Table II. These values were obtained as averages of the d spacings of the first three (001) reflections in each diffractogram. The interlayer spacings agree well with literature values [6, 8].

Thermogravimetric data were obtained for all of the preparations. A typical result for $Mg_{4.72}Al(OH)_{11.2}Cl_{0.94}(CO_3)_{0.15} \cdot 4.5\,H_2O$ (sample RW-56A) is shown in Figure 3. The derivative curve indicates that three separate weight losses occur. The first one, which is complete at approximately 240°C, is due to the loss of water, both surface water and water of crystallization. The total weight loss to this point is 17.2%. This compares to a calculated value, based on the formula in Table I, of 17.7%. The second weight loss is attributed to the loss of water by condensation of hydroxyl groups. However, only 5.13 moles of water can split out from the 11.2 moles of hydroxyl present (sample RW-56A) in order to preserve charge neutrality. According to the proposed formula in Table I this loss should amount to 20.29% as compared to the experimental curve which exhibits a value of 19.8% between 240–450°C. The final reaction is due to the removal of the interlamellar chloride (as HCl) and carbonate ions which amounts to 9.03% as opposed to a calculated value of 8.97%. These weight loss results are in good agreement with the relatively complete thermal analysis previously presented for the $Zn_2Cr(OH)_6X$ system [20].

In Table III are collected elemental analyses for several LDH which were exchanged (actually as we shall see both exchanged and intercalated) with dodecyl sulfate (DDS). The reactions were carried out by treating the sulfate with sodium hydroxide to a pH of 10 and then adding this solution to a slurry of the LDH. The ratio of DDS to LDH added was in all cases 2.05–2.08 times the anion content of the LDH. It is seen in Table III that not all of the chloride or carbonate ion was displaced by the organic sulfate even with this large excess of sodium dodecyl sulfate added. Moreover, sample RW-57D contained more than the amount required for charge neutralization. Thus, the additional organic must be present in

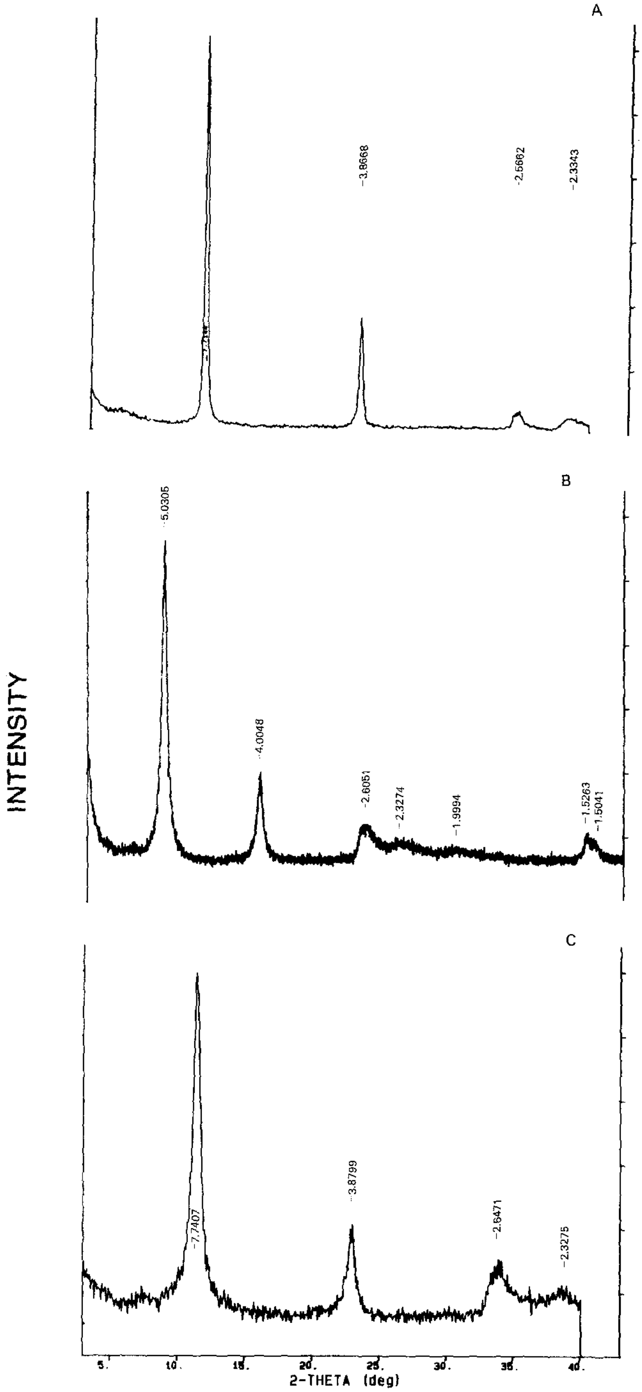


Fig. 2. Representative X-ray diffraction powder patterns of layered double hydroxides: (A) $Mg_2Al(OH)_6Cl \cdot 2\ H_2O$, (B) $Mg_5Al(OH)_{12}Cl \cdot 4.5\ H_2O$, (C) $Ni_2Al(OH)_6Cl \cdot 3.5\ H_2O$. [Formulas are idealized].

Table II. X-ray diffraction data for the layered double hydroxides.

Ni/Al/Cl Elemental Ratio	d_{003}(Å)	Mg/Al/Cl Elemental Ratio	d_{003}(Å)	Zn/Cr/Cl Elemental Ratio	d_{003}(Å)
2/1/1	7.77	2/1/1	7.74	2/1/1	7.81
3/1/1	7.84				
4/1/1	7.95				
5/1/1	7.97	5/1/1	8.00		
		Mg/Al/CO_3			
		5/1/1	7.85		

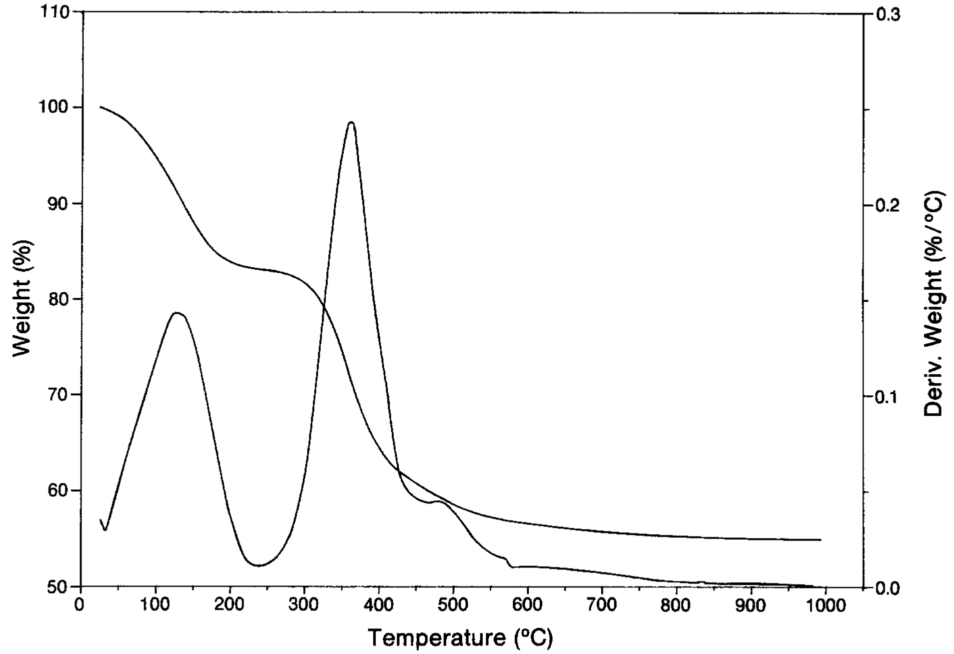


Fig. 3. A thermogravimetric curve for $Mg_{4.72}Al(OH)_{11.2}Cl_{0.95}(CO_3)_{0.15}\cdot 4.5\,H_2O$ (RW-56A). These results are representative of those obtained for other LDH which generally show three distinct weight losses.

the form of the sodium salt. Analysis for sodium gave a value of 1.25%. The infrared pattern indicated that no carbonate was present. The X-ray powder patterns of most of the samples containing DDS exhibited a single broad reflection whose basal spacing was in the range of 35–38 Å as shown in Figure 4B. This large interlayer spacing indicates a bilayer formation of the organic groups with a range of interlayer spacings. The exact interlayer spacing may depend upon the angle of tilt of the chains or the water content. One exception was sample RW-57D. This compound gave a spacing of ~26 Å even though it contained excess DDS and the peak was unsymmetrically skewed toward higher interlayer spacings. An infrared spectrum of a typical intercalated sample, RW-57A, is shown in Figure 5. This spectrum contains a large absorption band centered at 3500 cm^{-1} due to the

Table III. Elemental analysis of layered double hydroxides intercalated with dodecyl sulfate.

Sample No.	RW-57A		RW-57D		RW-2-60A		RW-2-60D	
Element	% obs	% Calc[a]	% obs	% Calc[b]	% obs	% Calc[c]	% obs	% Calc[d]
Mg	18.67	18.66	8.73	8.51	—	—	—	—
Ni	—	—	—	—	22.76	22.92	32.95	32.90
Al	4.28	4.28	4.71	4.70	5.27	5.26	3.15	3.15
S	4.24	4.22	7.02	7.01	4.54	4.54	3.18	3.18
H	6.33	5.99	7.79	7.46	6.23	6.12	5.27	5.39
Na	1.25	1.0	2.0	2.06	—	—	0.31	0.40
Cl	2.49	2.47	0.12	—	0.35	0.34	1.23	1.24
H_2O*	7.0	7.14	8.85	7.53	12.65	12.66	13.05	13.67

[a] Based on the formula $Mg_{4.84}Al(OH)_{11.68}Cl_{0.44}\cdot 0.56C_{12}H_{25}SO_4\cdot 0.274C_{12}H_{25}SO_4Na\cdot 2.5H_2O$.
[b] Based on the formula $Mg_2Al(OH)_6(CO_3)_{0.13}\cdot 0.74C_{12}H_{25}SO_4\cdot 0.515C_{12}H_{25}SO_4Na\cdot 2.4H_2O$
[c] Based on the formula $Ni_2Al(OH)_6(CO_3)_{11.2}Cl_{0.05}\cdot 0.725C_{12}H_{25}SO_4^-\cdot 3.6H_2O$.
[d] Based on the formula $Ni_{4.8}Al(OH)_{11.6}Cl_{0.3}\cdot 0.7C_{12}H_{25}SO_4\cdot 0.15C_{12}H_{25}SO_4Na\cdot 6.2H_2O$.
*From TGA.

metal hydroxyl and water O—H stretch and typical C—H stretching and bending modes and bands due to the SO_4 group. These are centered at 2957, 2924, 2852 cm^{-1} (C—H stretch), 1468 cm^{-1} (CH bend) 1246 and 1224 cm^{-1} (C—H twist and —SO_4), 1000 and 875 cm^{-1} (—SO_4). Many of these bands were identified from an infrared spectrum of the pure dodecyl sulfate. There is also a very broad band from about 500 to 800 cm^{-1} due to general metal–oxygen lattice vibrations which overlays the spectrum in this region.

A number of experiments were carried out in which the time and temperature of the reaction as well as the mole ratio of DDS to LDH was varied (from 0.1 to 2). In general, it was found that up to 1.5 moles of DDS could be incorporated into the interlamellar space. When the ratio was below 0.8, the products consisted of some unreacted LDH as well as the intercalated phase. This result was inferred from both X-ray diffractograms and infrared spectra. The IR spectra were similar to the one shown in Figure 5 except that the relative intensities of the C—H stretching vibrations and the SO_4 vibrations to both the —OH band at 3500 cm^{-1} and the broad M—O band were indicative of the amount of DDS intercalated. The X-ray patterns showed a very weak and disordered pattern for the LDH and a large amorphous band at low 2θ angle presumably resulting from that portion of the layered double hydroxide which contained most of the organic.

At high levels of intercalation (greater than a ratio of 0.8) X-ray patterns indicative of more ordered structures were obtained ranging from a single large peak for the interlayer spacing to those which gave 6–7 (001) reflections. Two sets of interlayer spacings were observed; one group was centered at 47 Å and the other, more common value, at 35 Å as already mentioned. Infrared patterns of the two sets were nearly identical. Elemental analyses were quite similar to those shown in Table III. Thus, the higher interlayer spacing must result from a somewhat different arrangement of the guest molecules within the interlamellar space.

TGA curves for two dodecylsulfate intercalates, RW57A and RW-2-60D, are shown in Figure 6. The nickel-aluminum compound exhibits 4 weight losses. Mass

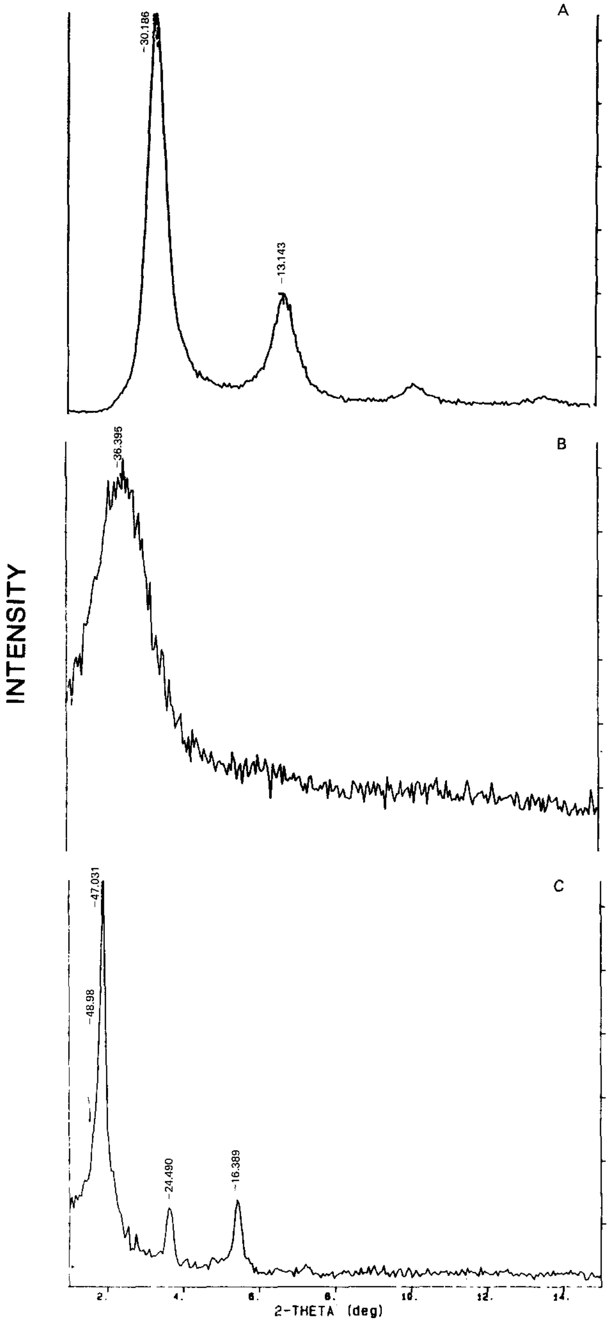


Fig. 4. Representative X-ray diffraction powder patterns of LDH exchanged (and intercalated) with dodecyl sulfate: (A) DDS incorporated *in situ* during preparation of $Ni_2Al(OH)_6X$, $d_{001} = 26.3$ Å (B) sample RW-2-60C, $Ni_3Al(OH)_8C_{12}H_{25}SO_4$(pH ~ 9). (C) $Ni_4Al(OH)_{10} \cdot C_{12}H_{25}SO_4 \cdot 3\ H_2O$ prepared at high pH (> 10).

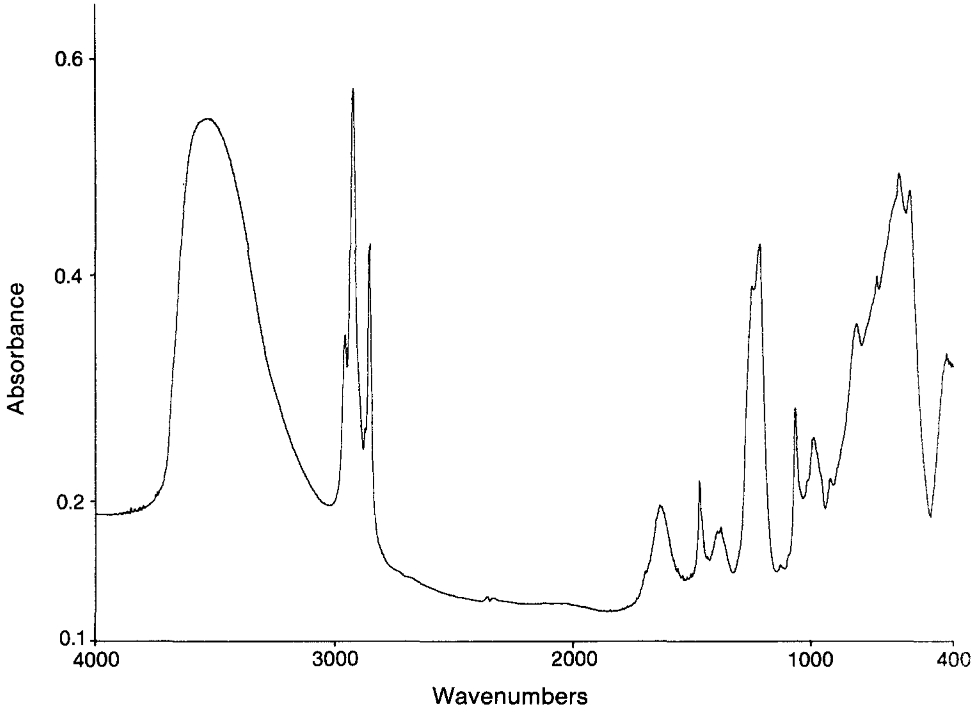


Fig. 5. Infrared spectrum of sample RW-57A (see Table III for formula).

spectroscopy up to 480°C was used to determine which gases were evolved. The different steps are depicted in Scheme 1. The initial weight loss amounts to 13.05% and is due to the loss of the interlamellar water. Calculated weight losses for each step are

Scheme 1 - Calculated Weight losses for sample RW-2-60D

$Ni_{4.8}Al(OH)_{11.6}Cl_{0.3} \cdot 0.7CH_3(CH_2)_{11}SO_4 \cdot 0.15\ CH_3(CH_2)_{11}SO_4Na \cdot 6.2H_2O$

13.04% $\downarrow$ 25-180°C

$Ni_{4.8}Al(OH)_{11.6}Cl_{0.3} \cdot 0.7CH_3(CH_2)_{11}SO_4 \cdot 0.15\ CH_3(CH_2)_{11}SO_4Na + 6.2H_2O$

16.7% $\downarrow$ 180-380°C

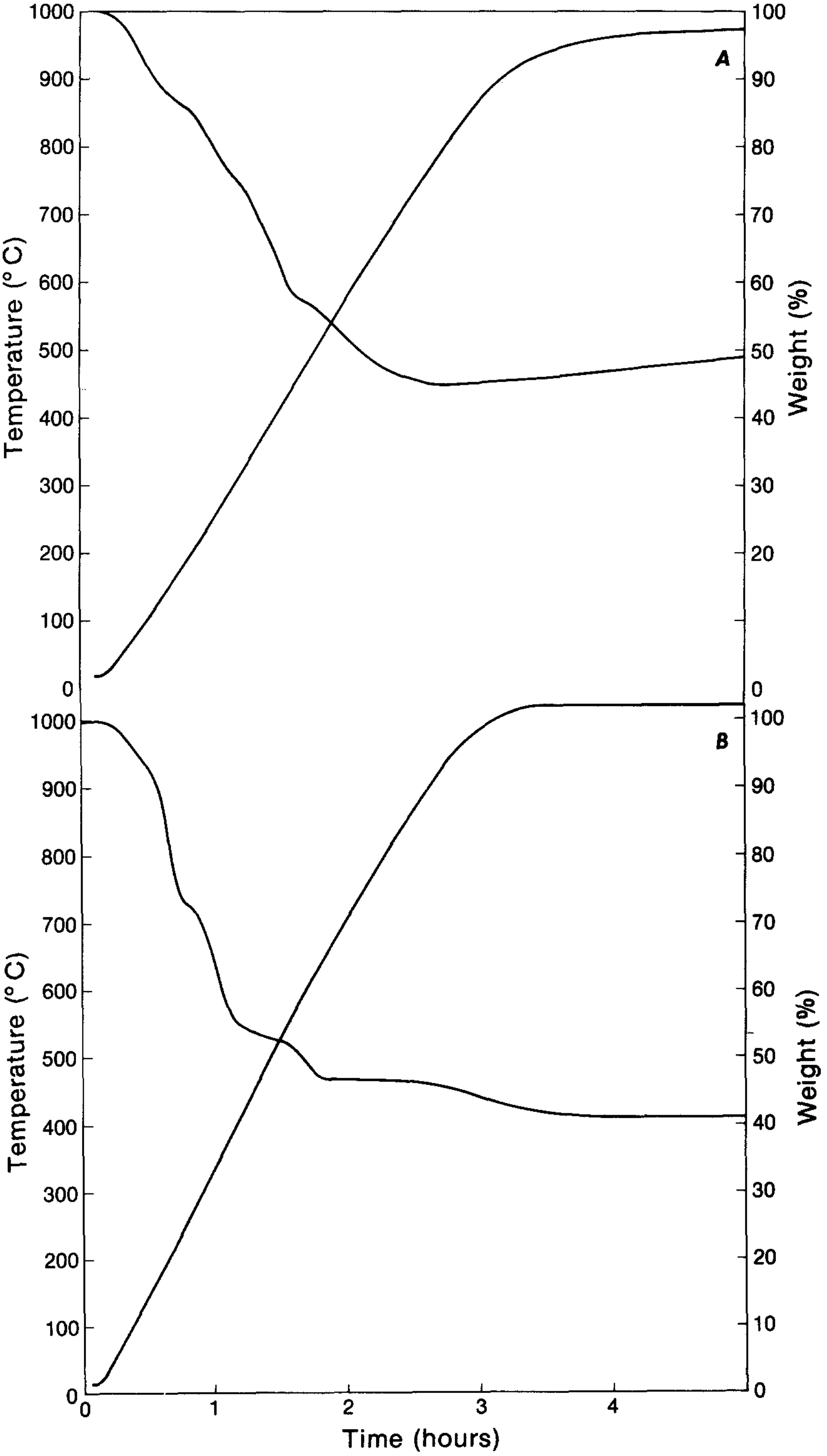
$Ni_{4.8}Al(OH)_{11.6}Cl_{0.3} \cdot 0.7HSO_4 \cdot 0.15NaHSO_4 + 0.85C_{12}H_{24}$

13.15% $\downarrow$ 380-500°C

$Ni_{4.8}AlO_{5.95}Cl_{0.3} \cdot 0.7HSO_4 \cdot 0.15NaHSO_4 + 5.65H_2O + 0.3HCl$

8.83% $\downarrow$ 500-950°C

$4.8NiO + 0.5Al_2O_3 + 0.0725Na_2O + 0.425H_2O + 0.85SO_3$


A
B
Temperature (° C)
Weight (%)
Time (hours)
1000
900
800
700
600
500
400
300
200
100
0
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4

next to the arrows for each step. At about 180°C a mass spectrogram showed that $C_{12}H_{24}$, mass 168, and its several decomposition products was evolving. No SO_3 or HCl was evolved up to 480°C the limit of temperature for our mass spectrometer system. The loss of organic amounted to 15.1%. From 380°C to 600°C a weight loss of 13.9% was observed which is attributed to split out of HCl and condensation of hydroxyl groups as H_2O. The final weight loss is then due to loss of SO_3 and water, leaving only a remainder of oxides. According to Scheme 1, the total calculated weight loss is 51.7% as compared to an observed value of 51.9%. The small differences in the calculated and observed weight losses probably result from an overlap of two processes. It should be noted though that the TGA curve dips to a minimum value of 55% at 780°C and then gains weight to 950°C. The presence of small amounts of carbon in the sample from incomplete combustion of the organic may bring about partial reduction of nickel followed by reoxidation to NiO. The presence of NiO and Al_2O_3 was observed in the X-ray diffraction pattern of the thermally treated sample.

Scheme 2 shows the different weight losses experienced by sample RW-57A. There are five distinct processes as recorded by the TGA curve (Figure 6B). Initially, approximately 7.0% is lost as water up to 150°C while the calculated value, in parenthesis in Scheme 2, is 7.14%. This is followed by removal of the organic portion of the dodecyl sulfate and at still higher temperature loss of hydroxyl water and HCl. In the next step, 525–630°C, SO_3 and water are lost but we indicate that the neutral sulfate remains, probably as magnesium sulfate, while the anionic sulfate is lost. The final step involves the decomposition of $NaHSO_4$.

Scheme 2 - Weight losses for sample RW-57A.

$Mg_{4.84}Al(OH)_{11.68}Cl_{0.44} \cdot 0.56CH_3(CH_2)_{11}SO_4 \cdot 0.27CH_3(CH_2)_{11}SO_4Na \cdot 2.5H_2O$

25-150°C ↓ 7.0% (7.14)

$Mg_{4.84}Al(OH)_{11.6}Cl_{0.44} \cdot 0.56CH_3(CH_2)_{11}SO_4 \cdot 0.27CH_3(CH_2)_{11}SO_4Na + 2.5H_2O$

150-300°C ↓ 21.7% (22.2)

$Mg_{4.84}Al(OH)_{11.6}Cl_{0.44} \cdot 0.56HSO_4 \cdot 0.27NaHSO_4 + 0.83C_{12}H_{24}$

300-525 °C ↓ 19% (18.6)

$Mg_{4.84}AlO_{6.06}0.56HSO_4 \cdot 0.27NaHSO_4 + 5.62H_2O + 0.44HCl$

525-630 °C ↓ 7.0% (7.91)

$Mg_{4.84}AlO_{6.06} \cdot 0.27\ NaHSO_4 + 0.56SO_3 + .28H_2O$

630-870°C ↓ 4.4% (3.8)

$4.84MgO + 1/2Al_2O_3 + 0.135Na_2O + .27SO_3 + .135\ H_2O$

Fig. 6. Thermogravimetric curves for (A) sample RW-2-60D as depicted in Scheme 1, (B) sample RW-57A as depicted in Scheme 2.

Table IV. Effect of pH of exchange upon the interlayer spacing of LDH · DDS.

Exp. No.	pH of Exchange Medium	Interlayer Spacing (Å)	Weight Losses (%)		
			180°C	350°C	900°C
36A	5	25.9	10.0	31	65.1
36B	6	26.8	9.4	29	62.9
36C	7	27.8	8.2	27.6	57.3
36D	8	28.4	7.3	26.9	56.0
36E	9	36.6	7.1	23.4	53.9
36F	10	42	9.9	22.5	52.6

Other members of the two LDH series behaved similarly.

X-ray diffraction patterns of samples prepared by incorporation of DDS in situ during the preparation of the LDH all showed that the interlayer spacing varied from 25 Å to 26.7 Å (Figure 4A). Elemental analysis of one of these samples gave the following results: Ni, 17.72%; Al, 4.19% S, 5.55%; C, 24.34%; H, 7.01%; Calculated for the formula $Ni_{1.94}Al(OH)_{5.88}{\cdot}CH_3(CH_2)_{11}SO_4{\cdot}0.115\ CH_3(CH_2)_{11}SO_3Na{\cdot}5.8\ H_2O$: Ni, 17.69%; Al, 4.19%, S, 5.55%; C, 24,96%; H 7.1%. It is evident from these results that the amount of dodecyl sulfate incorporated by the in situ procedure is similar to that obtained by other methods. Thus, the lower interlayer spacing is not due to the LDH containing less dodecyl sulfate but must result from a different arrangement of the guest molecules.

In a separate set of experiments, the dodecyl sulfate was intercalated at different pH values from 5 to 11. The pH was maintained constant by additions of either 0.1N HCl or 0.1N NaOH as required. X-ray powder patterns showed (Table IV) that as the pH at which exchange was carried out increased, so did the interlayer spacing. The LDH used in this series of experiments was $Ni_4Al(OH)_{10}Cl{\cdot}3\ H_2O$. The results of thermogravimetric analysis are also listed in Table IV. Since at 900°C it is expected that almost the same oxide mixture would remain, it is evident that the amount of dodecyl sulfate incorporated decreases with increasing pH. It is estimated from the TGA data that the sample prepared at pH 5 contained 1.8 moles of dodecyl sulfate while that obtained at pH 10 contained 0.9 moles. In spite of this differential the samples obtained at the lower pH has lower interplanar spacings.

In a final set of experiments, we attempted to remove the dodecyl sulfate by treatment of LDH·DDS with dilute (0.1N) HCl. Two LDH were chosen for study. In the first, the approximate composition was $Mg_3Al(OH)_8{\cdot}DDS{\cdot}3\ H_2O$. This solid (10g) was subjected to treatment with a total of 175 ml of the acid. The pH rose from about 4.24 on initial mixing to near neutral (pH = 6.75) in two hours. Of the 10 g original sample only 3.1 g of solid was recovered. Analysis of this solid is given in Table V (MK-2-05A). A second sample was treated the same way except that 291.7 mL of acid was used. In this case, only 2 g of solid was recovered. Analysis of this solid is also given in Table V (MK-2-05B). X-ray patterns for the recovered samples indicated that the solids were two phase mixtures. One phase, in the lesser amount, was the original LDH·DDS and the other phase, which had much sharper

Table V. Elemental analysis of layered double hydroxides—dodecyl sulfates after acid treatment.

Sample No.	MK-2-05A		MK-2-05B		MK-2-09		MK-2-10	
Element	% obs	% Calc[a]	% obs	% Calc[b]	% obs	% Calc[c]	% obs	% Calc[d]
Mg	5.50	5.48	1.78	1.78	—	—	—	—
Ni	—	—	—	—	18.45	18.45	13.80	13.81
Al	4.57	4.57	3.74	3.74	4.02	4.02	3.80	3.80
S	8.26	8.25	6.93	6.93	7.39	7.39	7.20	7.19
C	34.66	37.12	40.54	31.15	27.73	33.22	31.59	32.53
H	7.96	8.28	8.63	9.29	6.55	6.88	7.27	7.61

[a] $Mg_{1.33}Al(OH)_{4.66}\cdot CH_3(CH_2)_{11}SO_4\cdot 0.52CH_3(CH_2)_{11}SO_4H\cdot 2.66H_2O$.
[b] $Mg_{0.53}Al(OH)_{3.06}\cdot CH_3(CH_2)_{11}SO_4\cdot 0.56CH_3(CH_2)_{11}SO_4H\cdot 11.9H_2O$.
[c] $Ni_{2.11}Al(OH)_{6.22}\cdot CH_3(CH_2)_{11}SO_4\cdot 0.547CH_3(CH_2)_{11}SO_4H\cdot 0.2H_2O$.
[d] $Ni_{1.67}Al(OH)_{5.34}\cdot CH_3(CH_2)_{11}SO_4\cdot 0.594CH_3(CH_2)_{11}SO_4H\cdot 3.9H_2O$.

reflections, is attributed to the free acid, $C_{12}H_{25}SO_4H$ which tends to align itself in sheets in the solid state. It is interesting to note that with the 5A sample the initial value of the LDH phase interlayer spacing decreased from 36 Å to 25 Å by the acid treatment while that for the 5B sample reduced to only 33 Å.

Two samples of $Ni_3Al(OH)_8\cdot DDS\cdot 3\ H_2O$ were also treated similarly with acid and the results are given in Table V. However, with these samples the XRD patterns show a single phase of the LDH·DDS product with the first reflection at 26 Å. This result raises the interesting question as to whether the recovered solid is a rearranged version of the original layered double hydroxide with the new ratio of metals or whether it is the original LDH with metal atoms missing from the layer i.e., layers with large numbers of defects.

4. Discussion

This study has shown that exchange (and in some cases accompanied by intercalation) of dodecyl sulfate takes place to yield products in which the basal spacings range themselves about three mean values; 26 Å, 36 Å and 47 Å. These basal spacings do not depend upon the amount of dodecyl sulfate incorporated but rather on the method of preparation. For example, we have shown that as the pH of exchange increases so does the basal spacing but the amount of dodecyl sulfate incorporated in the interlamellar region (both by exchange and intercalation) decreased as the pH increased. Therefore, the differences observed must depend upon the way in which the alkyl sulfate is arranged between the layers. This topic has been treated by Lagaly *et al.* [19, 21].

To aid in deducing the geometry of the dodecyl sulfate molecules between the LDH layers we have resorted to chemical graphics modelling. The LDH layers were built using the crystallographic software package CRYSTALS [22a] and the unit cell dimensions and atomic parameters for the mineral sjogrenite [4, 23]. The structure of dodecyl sulfate was built up using the program COSMIC [22c] which minimizes the energy of a sketch of the structure drawn on the screen. Manipulation of the various structural parts was effected with the program MOGLI [22b] on

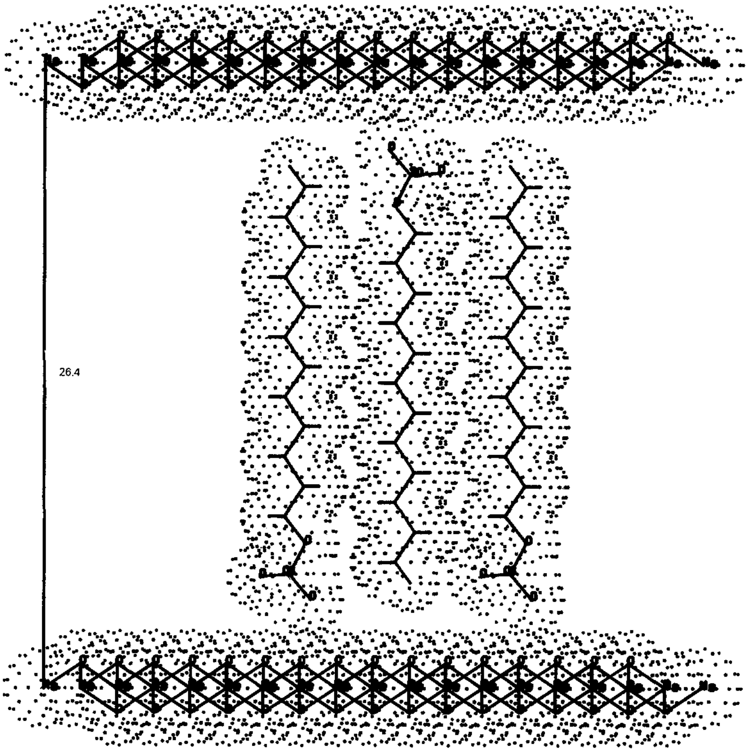


Fig. 7. Computer simulated representation of a layered double hydroxide (LDH) containing a monolayer of dodecyl sulfate anions: (A) front view (B) side view one chain wide. Dots represent the van der Waals surface.

the Evans and Sutherland PS 390 system. Figure 7 is the result of placing the dodecyl sulfate anions perpendicular to the LDH layer in a monolayer array. The polar ends of the chains are attracted to the positively charged LDH layers in alternating fashion and have been placed such that the interlayer spacing is 26.4 Å. Since the LDH layer thickness is 4.8 Å, the space occupied by the alkyl sulfate chains is 21.6 Å. The van der Waals end-to-end length of dodecyl sulfate, estimated from the crystal structure and chemical graphics is 20.8 Å [24]. Therefore, the dodecyl sulfate chains fit perfectly well within this space when standing in the perpendicular direction and the chains are in an all-*trans* conformation [21]. The LDH was assumed to have a stacking sequence of the hydroxyls in the *c* direction of AB—BA—AB—BA, as in the structure of the unintercalated LDH [4, 23]. This stacking sequence creates crevices in the interlayer region which can accommodate the dodecyl sulfate. In this position, the minimum basal spacing is $4.8 + 20.8$ or 25.6 Å. Previous researchers have observed similar interlayer distances for dodecyl sulfate exchanged LDHs [9, 16, 17, 18]. For example, Drezdon [9] reported an interlayer spacing of 26.3 Å for synthetic hydrotalcite. Iyagba [16] observed a basal spacing of 27 Å in his hydrotalcite studies while Boehm *et al.* [18] obtained a value of 26.15 Å for the zinc chromium LDH. Kopka *et al.* [19] reported a value of 26.0 Å for the latter LDH.

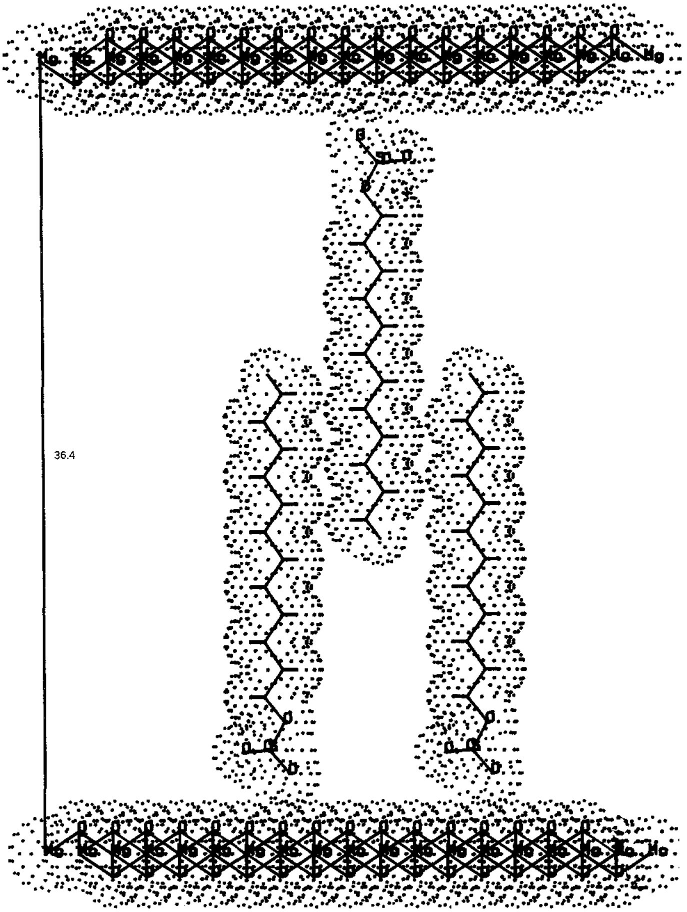


Fig. 8. Computer simulated representation of a bilayer arrangement of dodecyl sulfate chains in an LDH showing the degree of overlap required to achieve a basal spacing of 36.4 Å when the chains are perpendicular to the layers.

The products which had basal spacings in the neighborhood of 36 Å must contain bilayers of the dodecyl sulfate. There are two ways to represent the bilayer. Either the layers could be partially overlapped as shown in Figure 8 or they could be tilted in such a way that some or no overlap occurs. These figures show that if the chains were in the overlapped position, open spaces would arise between neighboring chains. This distance between dodecyl sulfate molecules in the same face would be 2 × 4.94 Å where 4.94 Å is taken as the van der Waals distance of the chains. A better packing arrangement and maximum van der Waals attractions would result if the adjacent chains did not overlap but were close packed. This would require that the chains in the upper and lower faces be at distances dictated by van der Waals contacts with each other but with no interpenetration. Since the van der Waals length of the dodecyl sulfate chain is 20.8 Å, the angle of tilt (relative to the perpendicular to the layers) required to yield a perpendicular distance of 15.8 Å per chain is $\sin^{-1}(15.8/20.8) = 49.4°$.

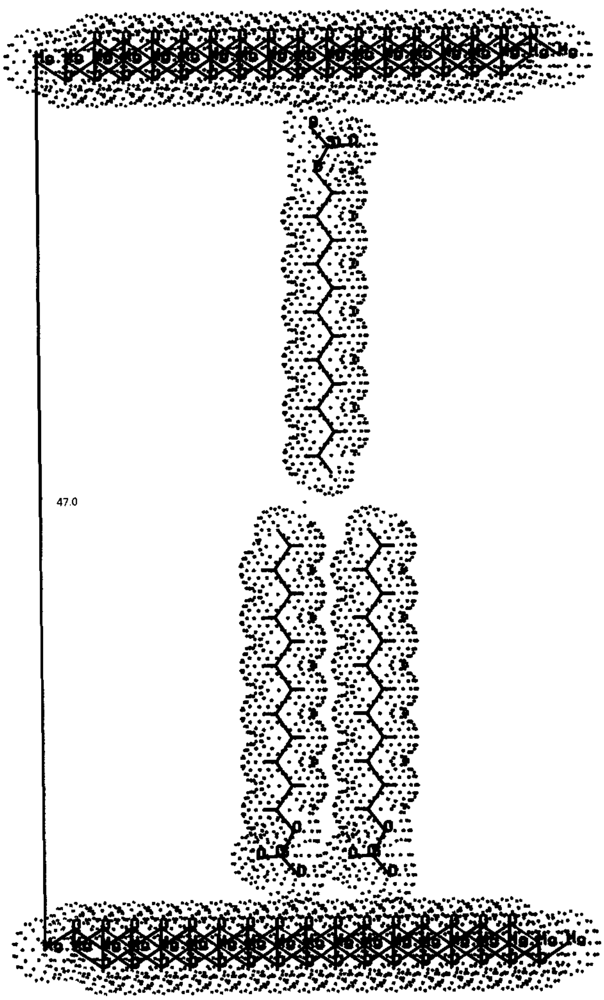


Fig. 9. Computer simulated representation of a bilayer arrangement of dodecyl sulfate chains in an LDH with basal spacing of 47 Å showing that the chains in the upper and lower surfaces are separated at greater than van der Waals distances

With this tilt the interlayer spacing is calculated to be 36.4 Å. The range of observed distances could then result from different angles of tilt or overlap. Ghabru *et al.* [25] recently proposed tilt angles of 49.3–59.1° for alkylammonium exchanged vermiculites with the exact tilt angle depending upon the layer charge density.

Placing the dodecyl sulfate chains perpendicular to the layers in a bilayer arrangement leads to a basal spacing of 46.4 Å. We have constructed the model shown in Figure 9 with a 47 Å interlayer spacing. If the chains were closely packed, there would be an excess of negative charge (see below) so that a number of the chains would have to be associated with sodium ions (or hydronium ions) to balance the charge.

In the models illustrated, it should be noted that a close packed bilayer will contain twice as much alkyl sulfate as the monolayer or interpenetrating bilayer model. Depending upon the layer charge such close packed arrangements could accommodate more anion than required by the layer charge and allow neutral sodium dodecyl sulfate chains to also be incorporated. A dodecyl sulfate molecule occupies 21.1 Å^2 of layer space in a hexagonal close packed arrangement [24]. The surface area per face of the LDH unit cell is 8.32 Å [4, 23]. Consider an LDH of formula $M(II)_2M(III)(OH)_6(X^-)$. One positive charge is spread over three brucite type unit cells or an area of $2 \times 3 \times 8.32$ Å^2 counting top and bottom of the layer. In the interpenetrating model the alkyl chain requires 42.2 Å^2 of surface. Therefore, a maximum of 1.18 moles of dodecyl sulfate can be accommodated per formula weight of LDH; one mole to satisfy the layer charge and 0.18 moles could be present as neutral salt. The amount of excess alkyl sulfate that could be accommodated in the interlamellar regions increases rapidly with increasing M(II)/M(III) ratio. For example, a ratio of 3 : 1 would allow incorporation of 1.58 moles of alkyl sulfate. In the bilayer model twice as much alkyl sulfate chains can be accommodated by the layers. Thus, there is sufficient room for water and neutralizing cations for the excess dodecyl sulfate.

Some of our exchanged samples did indeed contain more dodecyl sulfate than was required to satisfy the layer charge. For example, sample RW-57D contained 1.25 moles of dodecyl sulfate per formula weight but had a basal spacing of 26 Å. This value exceeds the limit of 1.18 moles calculated for a 2:1 LDH compound. One possible explanation for this discrepancy may stem from the large external surface area of layered double hydroxides. On the outer surfaces, the alkyl chains only cover one surface (as for a non-interpenetrating model) instead of two as when they are present between layers. This factor was not taken into account in the calculation. Thus, if the outer surface is 70 m^2/g and the M(II)/M(III) ratio is 2, the surface could accommodate $1/2 \times 70 \times \text{F.W.} \times 10^{20}$ Å^2/m^2 $\div$ (21.1 Å^2 $\pm 6.02 \times 10^{23}$) = 0.069 moles of additional dodecyl sulfate. Examination of sample RW-57D under the electron microscope showed that it consisted of particles which varied from 25 μm to 300 μm. However, higher magnification revealed that these particles were in effect aggregates of much smaller filamentous particles of a high degree of curvature. This arrangement imparted a highly porous character to the particles. The measured surface area was 244 m^2/g, more than enough to accommodate the excess dodecyl sulfate. However, the original LDH particles had a much lower surface area, in the range of 50 m^2/g. Thus, much of the increase must have occurred through the intercalation process and given rise to the unusual texture observed by electron microscopy. The nature of these surfaces and their texture including surface areas will form the subject of another paper, but the surface areas appear to be large enough to accommodate the excess alkylsulfate.

A second case to consider is that of $Ni_4Al(OH)_{10}Cl \cdot 3\,H_2O$ which at pH 5 was estimated to contain 1.8 moles of dodecyl sulfate. For this LDH the surface area per positive charge is 83.2 Å^2 so that 1.97 moles can be accommodated within the interlamellar space. All of the acid treated products contained about $1\frac{1}{2}$ moles of dodecyl sulfate but as indicated, these high values represent partial crystallization of solid dodecyl sulfate on to the surface of the LDH platelets.

In conclusion, we have shown that dodecyl sulfate can be incorporated into layered double hydroxides to form a variety of structures depending upon the experimental conditions. The models proposed here form a basis on which the various structures may be rationalized.

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