Chapter 2
INTERCALATION STUDIES IN ANIONIC CLAYS

In this chapter we discuss our exploration of the possibility of intercalating anions of weak acids into anionic clays. We also wanted to explore the possibility of exchanging strongly intercalated carbonate anion to get better ordered anionic clays. This chapter is divided into two sections. In section A, we discuss our work on exchanging strongly held carbonate anion with anions like nitrate and halides under ‘acid free’ conditions. In section B, we report our results on intercalating isomeric nitrophenolate ions in Mg-Al LDH.
Section A

‘Acid free’ deintercalative anion exchange of carbonate from carbonated layered double hydroxides

Deintercalation of carbonate from layered double hydroxides followed by intercalation (decarbonative intercalation) is a good method for the synthesis of ordered layered double hydroxides. We have carried out decarbonative intercalation of halides, nitrate and sulfate by refluxing the carbonated LDH with the corresponding ammonium salt in 1-butanol to obtain ordered LDHs incorporating the desired anion.
2.1 Introduction

Layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTLCs) can be represented by the general formula \([M^{2+}_{(1-x)}M^{3+}_x(OH)_{2}]^{3+}(A^{n-})_{x/n}m\text{H}_2\text{O}\), where \(M^{2+}\) is a divalent metal ion, \(M^{3+}\) is a trivalent metal ion and \(A^{n-}\) is the charge balancing interlayer anion [1]. Naturally occurring mineral hydrotalcite [2], whose formula is \(\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot4\text{H}_2\text{O}\), belongs to this class and has carbonate in its interlayer as the charge balancing interlayer anion. Carbonate anions are known to be held tenaciously in the interlayer which restricts its use in the synthesis of LDHs with other interlayer anions and thus chloride or nitrate containing LDHs are generally preferred as the starting precursors for the synthesis of other derived LDHs through anion exchange [3]. However this leads to products with low crystallinity and to obtain a higher degree of crystallinity the products are generally subjected to post synthesis hydrothermal treatment. Also, synthesis of LDHs with anion other than carbonate requires prevention of contamination due to carbonate from atmospheric carbon dioxide by a suitable method. Intercalation of a suitable anion into a layered solid depends upon its selectivity/affinity for the layered solid, there have been various studies about selective intercalation of organic [4-6] or inorganic [7] anions in layered solids, but it is well known that the selectivity of carbonate towards LDHs is very high, due to which its removal or intercalation of ions other than carbonate in its presence become difficult.

Various methods for the deintercalation of carbonate ion in order to obtain other anion intercalated LDHs with higher crystallinity have been reported. It was observed that when takovite was treated with cold dilute HCl, interlayer carbonate could be deintercalated and chloride anions got intercalated as seen from the infrared (IR) spectrum of the product which was similar to the parent solid except that the carbonate peaks were absent and the powder X-ray diffraction (PXRD) pattern of the product was slightly modified with the basal spacing changed to 7.70 Å [8]. Decarbonative intercalation of chloride could be achieved by passing a stream of water vapour and gaseous HCl through hydrotalcite sample maintained at 140-160 °C in a glass tube [9].

It was found that the decarbonation was better in the presence of a salt with a common anion as that of the dilute acid used [10]. It was proposed that deintercalation is enhanced due to the protonation of carbonate ions in the interlayer space and
subsequent ion exchange with a large excess of Cl$^-$ ions present in solution. However, here the decarbonated product showed small peaks due to carbonate ion in the IR spectrum. It was found that decarbonation of carbonate-LDH is highly enhanced by adding NaCl to a dilute HCl solution to obtain chloride intercalated LDH and that 0.005 N HCl with 13 weight percent of NaCl was required to obtain a pure chloride intercalated LDH [11]. It was easier to decarbonate $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)^{-}\cdot\text{mH}_2\text{O}$ compared to carbonate richer $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)^{-}\cdot\text{mH}_2\text{O}$. While the decarbonation of the former could be achieved with a NaCl concentration of ~2 mol/L the latter required a NaCl concentration of >4 mol/L and it proceeded slower than in the case of the former [12]. When using salt-acid mixed solution for decarbonation, almost complete substitution of carbonate ions was possible for the Cl$^-$ and Br$^-$ ions but with the I$^-$, NO$_3^-$ and ClO$_4^-$ ions a complete decarbonation was not possible even at high salt concentrations [13].

Subsequently Iyi’s group [14] used acetate-buffer/NaCl mixture to obtain good quality Cl-LDH. Later they studied the decarbonation of carbonated LDH using acetate buffer/salt mixture, in a closed vessel and under N$_2$ flow [15]. It was found that N$_2$ flow gives better decarbonation and requires lower concentration of the salt for complete decarbonation.

LDHs find applications in various fields as catalysts, scavengers, biosensors, polymer composites, etc. to name a few. Preparation of a composite usually involves delaminating a layered solid in a suitable solvent [16], followed by the composite preparation. Delamination of carbonated LDHs would be preferred as synthesis of particles with larger size is easy for carbonate than for other anions. Hayashi and Nakayama reported direct intercalation of organic acids, captopril and lipoic acid and inorganic chloride and nitrate anions into a carbonated LDH using alcohol as solvent [17]. Though the intercalation was carried out using a large excess of anions (240 mmoles of NaNO$_3$ and 150 mmoles of NaCl per gram of the LDH) there was still carbonate present in the final products. It has been shown that acid-alcohol mixed solutions could be used for decarbonation of LDHs to form the LDH intercalated with the corresponding conjugate base of the acid used [18].

There are two reports on ‘acid free’ decarbonative intercalation reactions in LDHs. Decarbonation and delamination of carbonated LDH was achieved in a 1:1 (v/v) DMF-ethanol solvent mixture, which lead to the formation of formate
intercalated LDH [19]. Carbonate could be exchanged by anions like $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and Cl by heating the carbonated LDH in glycerol containing the salt of the anion to be intercalated at 160 – 180°C [20].

In the IR spectrum of MgAl-CO$_3$ LDH heated to 100°C the water-carbonate IR absorption appearing around 3165 cm$^{-1}$ disappeared and the anti-symmetric stretching mode $\nu_3$ of carbonate appearing at $\sim$ 1365 cm$^{-1}$ split into two bands at 1357 and 1391 cm$^{-1}$ and a sharp band around 1538 cm$^{-1}$ appeared which indicated a change in the carbonate symmetry upon dehydration of the hydrotalcite at 100°C [21]. The loss of water molecules breaks the H-bonding network and weakens the bonding of interlayer carbonate with the layers. Olanrewaju et al. [22] reasoned that presence of ammonia in solution prevents carbonate from getting intercalated into the interlayer of LDH, as seen by them during their modified synthesis of nitrated-LDH. Keeping these in mind, we have carried out decarbonative anion exchange using ammonium salt of the anion of interest (ammonium chloride, ammonium nitrate and ammonium sulfate) at 120°C in 1-butanol. This procedure is shown to be a general method for the synthesis of desired LDHs with better crystallinity from carbonate LDHs in a single step.

2.2 Experimental

2.2.1 Synthesis of MgAl LDH, Mg$_2$Al(OH)$_6$(CO$_3$)$_{0.5}$·2H$_2$O and NiAl LDH, Ni$_2$Al(OH)$_6$(CO$_3$)$_{0.5}$·2H$_2$O

The carbonated LDH, Mg$_2$Al(OH)$_6$(CO$_3$)$_{0.5}$·2H$_2$O, was prepared by modifying the method reported by Reichle [23]. 1.00 mol of magnesium nitrate, Mg(NO$_3$)$_2$·6H$_2$O and 0.50 mol of aluminum nitrate, Al(NO$_3$)$_3$·9H$_2$O in 0.70 L of water was added drop wise under vigorous stirring, to 1 L of an aqueous solution containing 3.5 mol of sodium hydroxide and 1.67 mol of sodium carbonate. After the addition was complete, the material obtained was hydrothermally treated at 70 °C for 18 h, washed with water and dried at 65 °C in an air oven to constant weight. Ni$_2$Al(OH)$_6$(CO$_3$)$_{0.5}$·2H$_2$O LDH was prepared in a similar way by adding a solution containing 0.03 mol of nickel nitrate, Ni(NO$_3$)$_2$·6H$_2$O and 0.015 mol of aluminum nitrate, Al(NO$_3$)$_3$·9H$_2$O into 50cm$^3$ of a solution containing 0.11 mol of sodium hydroxide and 0.05 mol of sodium carbonate. The material obtained was hydrothermally treated at 130 °C for 48 h. The product was then washed with deionized water and dried at 65 °C in an air oven to constant weight.
2.2.2 Synthesis of nitrate MgAl LDH Mg₂Al(OH)₆(NO₃)·2H₂O

The nitrate LDH, Mg₂Al(OH)₆(NO₃)·2H₂O, was prepared as a control sample by the method due to Olanrewaju et al. [22]. 1.00 mol of magnesium nitrate, Mg(NO₃)₂·6H₂O and 0.50 mol of aluminum nitrate, Al(NO₃)₃·9H₂O in 0.01 L of boiled and cooled distilled water was added drop wise, under vigorous stirring, to 0.09 L of a 1M aqueous ammonia solution. After the addition was complete, the material obtained was washed five times with boiled and cooled distilled water, and finally with acetone and dried at 65 °C in an air oven to constant weight.

2.2.3 Anion exchange reactions of carbonate LDHs with various anions

For achieving nitrate exchange in hydrotalcite 500 mg of the Mg₂Al(OH)₆(CO₃)₀.₅·2H₂O LDH was dispersed in 80 cm³ of 1-butanol containing 690 mg of ammonium nitrate [8.6 mmoles, a 8.4 times excess of the anion exchange capacity] in a round bottom flask and the solution was refluxed for 20 h. The refluxed sample was washed by centrifugation using acetone twice, once with fresh MilliQ water and finally once with acetone and then dried in an air oven at 65 °C to constant weight. Same procedure was followed for the exchange by other anions, except for the amount of ammonium salt used. For chloride exchange 650 mg of ammonium chloride [12.1 mmoles, a 11.8 times excess of the anion exchange capacity], for sulfate exchange 810 mg of ammonium sulfate [6.1 mmoles, 6 times excess of the anion exchange capacity], for bromide exchange 611 mg of ammonium bromide [6.2 mmoles, a 6 times excess of the anion exchange capacity], for iodide exchange 1188 mg of ammonium iodide [6.1 mmoles, a 8 times excess of the anion exchange capacity] and for acetate exchange 907 mg of ammonium acetate [11.77 mmoles, a 11.5 times excess of the anion exchange capacity] were used. Similar exchange reactions of NiAl LDH were also carried out.

2.2.4 Characterization

Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical Xpert Pro X-ray Diffractometer using Cu-Kα radiation (λ = 0.154 nm) at 40 kV, at a scanning rate of 2° min⁻¹. The infrared (IR) spectra of samples were collected using a Nicolet IR200 FT-IR spectrometer using KBr pellets, in the range 4000 to 400 cm⁻¹ with 4 cm⁻¹ resolution.
2.3 Results and Discussion

Success of the decarbonative anion exchange in LDHs can be corroborated from the changes observed in basal spacing along with the IR spectra of the final products. In Figure 2.1 the PXRD pattern of the starting carbonate intercalated MgAl LDH [hydrotalcite] is compared with those of the products obtained on decarbonative anion exchange. The d-spacing of the starting hydrotalcite 7.7 Å, changes to 8.8 Å for MgAl-nitrate, 7.8 Å for MgAl-chloride and 8.9 Å for MgAl-sulfate obtained through decarbonation of the starting hydrotalcite using their corresponding ammonium salts, confirming the conversion of the carbonated LDH to the desired anion intercalated LDH.

![Figure 2.1](image.png)

**Figure 2.1** PXRD patterns of carbonate intercalated MgAl layered double hydroxide [hydrotalcite] (a), MgAl-nitrate (b), MgAl-chloride (c) and MgAl-sulfate (d) LDHs obtained through decarbonative intercalation of the starting hydrotalcite.

This can also be confirmed from their IR spectra shown in Figure 2.2 In Figure 2.2(a) the characteristic IR absorption observed around 3070 cm$^{-1}$ for the carbonate [24] intercalated LDH is due to the – OH stretching of interlayer water arising from the strong interaction between interlayer water and the carbonate ion. The band around 1365 cm$^{-1}$ can be attributed to the anti-symmetric stretching mode $\nu_3$. 
of carbonate and bands observed around 870 and 678 cm\(^{-1}\) are attributed to the weak non-planar bending mode \(\nu_2\) and the angular bending mode \(\nu_4\) of carbonate respectively. The characteristic IR absorption peak for the nitrate which can be attributed to the very strong antisymmetric stretching mode \(\nu_3\) of nitrate [24] anion (Figure 2.2b) present in the LDH is observed around 1380 cm\(^{-1}\). The bands observed around 833 and 674 cm\(^{-1}\) can be attributed to the weak out-of-plane deformation symmetric mode bending mode \(\nu_2\) and the antisymmetric deformation mode \(\nu_4\) of nitrate respectively. In addition, the absence of the characteristic absorption around 3070 cm\(^{-1}\) confirms the absence of carbonate in the interlayer.

**Figure 2.2** IR spectra of carbonate intercalated MgAl layered double hydroxide [hydrotalcite] (a), MgAl-nitrate (b), MgAl-chloride (c) and MgAl-sulfate (d) LDHs obtained from decarbonation of the starting hydrotalcite.

In Figure 2.2(c) the IR spectrum of chloride exchanged LDH does not show any characteristic absorption peaks as the chloride ion is IR inactive, but its presence can be indirectly confirmed from the absence of absorption due to the starting carbonate. The IR absorption observed in 2.2(d) at 1126 cm\(^{-1}\) can be attributed to stretching mode \(\nu_3\) of sulfate and the weak bands observed around 614 and 981 cm\(^{-1}\) can be attributed to weak bending modes \(\nu_2\) and symmetric stretching mode \(\nu_1\) respectively for the sulfate anion present in the LDH [24].
Similar changes were observed when the decarbonative anion exchange was carried out for NiAl-CO$_3$-LDH. In Figure 2.3 PXRD patterns of carbonate intercalated NiAl layered double hydroxide and its ion exchanged products obtained through decarbonation are shown. Here the basal spacing of 7.6 Å for the starting carbonated NiAl-LDH, changes to 8.9 Å for NiAl-nitrate, 7.8 Å for NiAl-chloride and 8.7 Å for NiAl-sulfate.

![PXRD patterns](image)

**Figure 2.3** PXRD patterns of carbonate intercalated NiAl layered double hydroxide (a) NiAl-nitrate (b), NiAl-chloride (c) and NiAl-sulfate (d) LDHs obtained through decarbonative intercalation of the starting hydrotalcite.

Figure 2.4 shows the IR spectra of carbonate intercalated NiAl layered double hydroxide and the anion exchanged products obtained through decarbonation. There IR absorptions are similar to those of Mg-Al LDH samples and confirm the anion exchange except in the case of sulfate, where there is a slight carbonate contamination which might have occurred during the drying process due to the different hydration possibilities in sulfated LDH which might have helped atmospheric carbonate to enter.
Figure 2.4 IR spectra of carbonate intercalated NiAl layered double hydroxide (a) NiAl-nitrate (b) and NiAl-chloride (c) and NiAl-sulfate (d) LDHs obtained through decarbonation of the starting hydrotalcite.

Figure 2.5 PXRD patterns of carbonate intercalated MgAl layered double hydroxide [hydrotalcite] (a), MgAl-nitrate obtained from decarbonation of the starting hydrotalcite (b) and MgAl-nitrate obtained from ammonia precipitation method (c).
One of the advantages of decarbonative intercalation is that the ion-exchanged products are usually more crystalline [10] with fewer stacking disorders. To confirm if we could get ordered LDHs we compare the PXRD patterns of the MgAl nitrate LDH obtained through decarbonation and the same obtained by direct coprecipitation in Figure 2.5. It can be seen that the nitrated LDH obtained from decarboxylative anion exchange is more ordered than that synthesized by coprecipitation using ammonia solution. The order along the stacking direction in the ion-exchanged product is comparable to that of the starting hydrotalcite as suggested by similar peak broadening for the non-00l reflections.

![Figure 2.6 PXRD patterns of MgAl-chloride (a), MgAl-bromide (a) and MgAl-iodide (c) obtained through decarbonative intercalation of hydrotalcite.](image)

One of the shortcomings of the earlier decarbonation procedures is that they work well for nitrate and chloride exchange. In the case of bromide and iodide they could achieve only partial intercalation. Our method overcomes this shortfall and all the halide ions could be quantitatively intercalated. The PXRD patterns of Mg-Al-halides obtained by decarbonative intercalation of hydrotalcite are shown in Figure 2.6. The decarbonation is successful even in the case of large anions like bromide and iodide as seen from the shift in the first basal reflection. The reversal in the intensities...
of the first and second reflections as we move from chloride to bromide to iodide is seen, which is as expected due to the increase in the electron density in the midplane of the interlayer due to the change in the interlayer anion as we move from lighter chloride to heavier iodide.

In the IR spectra of the halide exchanged products shown in Figure 2.7 carbonate absorptions are absent indicating quantitative removal of carbonate ion.

![IR spectra](image)

**Figure 2.7** IR spectra of MgAl-chloride (a), MgAl-bromide (b) and MgAl-iodide (c) obtained through decarbonative intercalation of hydrotalcite.

### 2.4. Conclusions

We have been able to deintercalate carbonate from MgAl and NiAl LDH and replace it with monovalent anions like nitrate, chloride, bromide and iodide and a divalent sulfate anion showing the versatility of the method. The method does not use acid and the products obtained are well ordered along the stacking direction. This method is superior compared to existing methods since larger anions such as bromide and iodide could also be intercalated completely.
References


Section B

Intercalation of isomeric nitrophenolates into Mg-Al Layered Double Hydroxide: an investigation of preferential intercalation

Intercalation of the three isomeric nitrophenolate (NP) ions in Mg-Al LDH was studied. While 2-NP and 4-NP could be intercalated in the LDH 3-NP could not be intercalated. From a mixture of these isomeric anions 4-NP was preferentially intercalated in Mg-Al LDH. The failure of 3-NP to intercalate may be attributed to its high basicity which causes protonation induced deintercalation during washing. Between 4-NP and 2-NP, 4-NP intercalates better since its nitro group end can form H-bonds with the OH groups of the next layer.
2.5 Introduction

Phenol and its derivatives are used as antiseptics, in the synthesis of dyes, drugs, pesticides and herbicides [1]. Phenol is discharged from these industries into the water bodies affecting the water quality adversely [2]. Various methods such as oxidation [3], ultrafiltration [4], biodegradation and adsorption technique are available for the removal of phenol and its derivatives. Adsorption technique is the most widely used method and organically modified smectite clays have been used for phenol sorption [5]. Phenol, 2-nitrophenol (2-NP), 4-nitrophenol 4-(NP) and 2,4-dinitrophenol (2,4-DNP) have been adsorbed on carbon nanospheres (CNS) at various pH and ionic strengths [6]. It was found that a low pH (pH = 3) and presence of neutral electrolytes like NaCl in solution which decreases the solubility of the phenols in water increase the sorption of phenols [6]. Sorption of trichloro- and trinitro-phenol [7]; and adsorption of phenol and nitrophenol [6] by MgAl-mixed oxides derived from Mg-Al-LDH have been reported.

Preferential intercalation of 4-NP and 2,4-DNP in [LiAl$_2$(OH)$_6$]Cl·xH$_2$O (Li-Al-Cl LDH) has been studied by Ragavan et al [8]. They were able to intercalate 4-NP and 2,4-DNP into the Li-Al-Cl LDH, but were unable to intercalate 2-NP or 3-NP into the LDH under any of their experimental conditions and thus this preferential intercalation was used to achieve a separation of 4-NP from a mixture of 2-NP, 3-NP and 4-NP. They studied the competitive intercalation between 4-NP and 2,4-DNP too and they found that the intercalation of 4-NP was kinetically faster than that of 2,4-DNP. However from a equimolar binary mixture of 2,4-DNP and 4-NP, 2,4-DNP preferentially intercalates over 4-NP into Li-Al-Cl LDH. The effect of solvent on the preferential intercalation of 4-NP and 2,4-DNP was also studied in solvent mixtures (50:50 V/V) of water and a miscible polar solvents such as THF, acetone, ethanol, acetonitrile and DMSO. It was found that the percentage of intercalated 2,4-DNP with respect to 4-NP at 80 °C increases proportional to the dielectric constant of the solvent system. The two were equally intercalated in THF, where as in water 70% of 2,4-DNP was selectively intercalated into Li-Al-Cl LDH.

In this section we describe our studies on the intercalation of 2-NP, 3-NP and 4-NP in Mg$_2$Al(OH)$_6$(NO$_3$)$_2$H$_2$O layered double hydroxide (Mg-Al-NO$_3$ LDH) followed by their competitive intercalation involving an equimolar mixture of any two isomers.
2.6 Experimental

2.6.1 Synthesis of Mg-Al layered double hydroxide, Mg$_2$Al(OH)$_6$(NO$_3$)$_2$·2H$_2$O

Mg$_2$Al(OH)$_6$(NO$_3$)$_2$·2H$_2$O, Mg-Al LDH was prepared by the method due to Olanrewaju et al [10]. 1.00 mol of magnesium nitrate, Mg(NO$_3$)$_2$·6H$_2$O and 0.50 mol of aluminum nitrate, Al(NO$_3$)$_3$·9H$_2$O in 0.010 dm$^3$ of boiled and cooled distilled water was added drop wise, under vigorous stirring, to an aqueous ammonia solution containing a slight excess of the base in 0.090 dm$^3$. After the addition of mixed metal nitrates was complete, the resultant slurry was stirred for an additional 30 min. The white solid obtained was then separated by centrifugation and was washed five times with boiled and cooled deionized water, finally with acetone and dried at 65 °C in an air oven to constant weight.

2.6.2 Intercalation of nitrophenolate anions

Intercalation of the individual nitrophenolates was carried out using 3.0 mmol of the appropriate nitrophenolates dissolved in 50 ml of 1:1 (v/v) mixture of isopropyl alcohol (IPA) and 0.5 M aqueous ammonia solution. 500 mg of Mg-Al-NO$_3$ LDH was added to the above solution and the mixture was stirred for a period of 2 days. The solid product obtained was washed by centrifugation using cold deionized water five times and once with acetone before drying in an air oven at 65 °C to constant weight.

2.6.3 Preferential intercalation of nitrophenolate anions

Preferential intercalation studies were carried out by taking a solution containing 1.5 mmoles of any two nitrophenolates dissolved in 50 ml of 1:1 (v/v) mixture of IPA and 0.5 M ammonia solution. 500 mg of Mg-Al-NO$_3$ LDH was added to the above solution and stirred for a period of 2 days and the solid product obtained was washed by centrifugation using boiled and cooled deionized water five times and once with acetone before drying in an air oven at 65 °C to constant weight.

2.6.4 Characterization

The solid samples were characterized by Powder X-ray diffraction (PXRD) and infrared (IR) spectroscopy as described in section 2.2.4.
2.7 Results and Discussion

Intercalation of the large nitrophenolate ions into the LDH can be ascertained from the change in the basal spacing observed for the product LDHs. In Figure 2.8, the PXRD pattern of the starting nitrate intercalated Mg-Al layered double hydroxide is compared with those of the products obtained on anion exchange of the starting Mg-Al-nitrate LDH with the different nitrophenolate ions in IPA:water (50:50) mixture.

![PXRD patterns of nitrate intercalated Mg-Al LDH (a) and its anion exchanged products: 2-nitrophenolate (b), 3-nitrophenolate (c) and 4-nitrophenolate (d).](image)

The basal spacing for the starting Mg-Al-nitrate layered double hydroxide was 8.9 Å, which matches well with the value reported in literature for nitrate intercalated LDH [5]. An increase in the basal spacing to 15.0 Å and 16.4 Å was observed for the products obtained on anion exchange with 2-NP and 4-NP respectively. The increased basal spacing confirms the intercalation of the large nitrophenolate ions. The gallery heights in these cases are 11.5 Å and 11.9 Å and these match with the sizes of these ions. In the case of 3-NP the basal spacing does not change from that of the parent nitrate LDH used, indicating the possibility of 3-NP not getting intercalated into the LDH. It can also be seen that the product obtained in the case of 4-NP is more ordered than in the case of 2-NP as was generally observed for isomeric benzoates with the 4-
isomer producing the purest intercalation compounds, while the 2-isomers produced the most impure compounds [11].

**Figure 2.9** IR spectra of nitrate intercalated Mg-Al LDH (a) and its anion exchanged products: 2-nitrophenolate (b), 3-nitrophenolate (c) 4-nitrophenolate (d).

IR spectra of nitrophenolate exchanged products are compared with that of nitrate intercalated LDH in Figure 2. The bands appearing at 1358 and 1610 cm\(^{-1}\) for 2-NP exchanged product; and 1348 and 1597 cm\(^{-1}\) for 4-NP exchanged product can be assigned to the anti-symmetric and symmetric stretching vibrations of conjugated NO\(_2\) group. In addition bands appearing around 1544 and 1499 cm\(^{-1}\) in the spectrum of the former and, 1428, 1460 and 1502 cm\(^{-1}\) for the latter correspond to C=C bond vibrations of the aromatic ring. We observe a band at 749 cm\(^{-1}\) for the 2-NP exchanged LDH which can be attributed to the out of plane C–H vibration of an ortho disubstituted benzene ring while the bands appearing at 852 and 761 cm\(^{-1}\) for the 4-NP exchanged LDH can be attributed to the out of plane C–H vibration of a para disubstituted benzene ring [8]. The IR spectrum of the 3-NP exchanged product is the same as that of the parent nitrate intercalated LDH, in which a strong absorption around 1385 cm\(^{-1}\) can be attributed to the \(\nu_3\) antisymmetric stretching mode for the nitrate present in the LDH [12]. It can be confirmed from both PXRD and IR studies that 3-NP does not get intercalated into the LDH.
Figure 2.10 PXRD patterns of products obtained after the competitive intercalation of 2- and 3-nitrophenolates (a), 3- and 4-nitrophenolates (b) and 2- and 4-nitrophenolates (c) in Mg-Al-NO₃ LDH.

After ascertaining intercalation of individual nitrophenolate ions in the LDH we wanted to see if there is preferential intercalation of one of the isomers from a mixture into the LDH. PXRD pattern of the product obtained after the competitive intercalation of 2- and 3-NP (Figure 2.10a) we observe a small peak corresponding to the basal reflection of the 2-NP intercalated LDH. Otherwise the pattern is similar to that of the starting Mg-Al-NO₃ LDH. The pattern of the product obtained when the LDH was stirred in a solution containing a mixture of 3-NP and 4-NP (Figure 2.10b) matches exactly with 4-NP intercalated LDH (Figure 2.8d) suggesting that 4-NP is preferentially intercalated. In the pattern of the product obtained in the competitive intercalation of 2-NP and 4-NP (Figure 2.10c) we observe reflections due to 4-NP intercalated LDH and the starting LDH. It can be seen that when the 4-isomer is present it gets preferentially intercalated, while in the case when 2-NP and 3-NP are taken the observed basal spacing is almost the same as that of the precursor LDH.
In Figure 2.11 IR spectra of products obtained after the competitive intercalation reactions are shown. In the case of competition between 3- and 4-NP (Figure 2.11b) and 2- and 4-NP (Figure 2.11c) the IR spectrum of the product shows bands appearing at 1350, 1597, 1421, 1460 and 1501 cm\(^{-1}\) corresponding to 4-NP. Also the bands observed at 852 and 762 cm\(^{-1}\) can be attributed to the out of plane C–H vibration of a para disubstituted benzene ring. These confirm that the preferential intercalation of 4-NP occurs when it is present along with 2-NP or 3-NP. In the competition between 2-NP and 3-NP, 2-NP gets intercalated into the LDH which can be seen from the IR spectrum of the product (Figure 2.11a). In Figure 2.11a we observe bands appearing at 1356, 1610, 1544 and 1499 cm\(^{-1}\) which correspond to 2-NP. Also a band is observed at 747 cm\(^{-1}\) which can be attributed to the out of plane C–H vibration of an ortho disubstituted benzene ring. These confirm the preferential intercalation of 2-NP when present along with 3-NP.

The preference of the nitrophenolates to intercalate in the LDH is in the order 4-NP > 2-NP >> 3-NP. While 3-NP is not intercalated at all 4-NP is almost 100% selectively intercalated from a mixture of 4- and 2-NP.
2.8 Conclusions

We were able to intercalate 2-NP and 4-NP into Mg-Al LDH while 3-NP could not be intercalated under the experimental conditions used by us. The preference for intercalation of the three isomeric nitrophenolates is in the order 4-NP > 2-NP >> 3-NP. While the fact that nitrophenols can be intercalated can be made use of in the removal of these pollutants from water bodies, the preferential intercalation offers a method to separate the three isomers from their mixture.

References: