Aging of trivalent metal hydroxide/oxide gels in divalent metal salt solutions: Mechanism of formation of layered double hydroxides (LDHs)

A V RADHA and P VISHNU KAMATH*

Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

Abstract. While the aging of freshly precipitated $Al(OH)_3$ gels in solutions of Mg and Ni salts leads to LDH formation at high (> 12) pH, aging of '$Fe(OH)_3$' leads to LDH formation in Mg salt solutions but not in Ni salt
$_3$' gels do not form LDHs on aging in any of the divalent metal salts. In general, conditions that promote the re-dissolution of the trivalent hydroxide also promote LDH formation showing that oxoanionic species such as AlO_2^- have a role in LDH formation.

**Keywords.** Layered double hydroxides; pH metric titrations.

1. Introduction

Layered double hydroxides (LDHs) having the general formula, $[M(II)_{1-x}M'(III)_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, are a class of compounds derived from the structure of mineral brucite, $Mg(OH)_2$ (Cavani *et al* 1991). Brucite comprises a hexagonal packing of hydroxyl ions, in which Mg^{2+} ions occupy alternate layers of octahedral sites, leading to a stacking of charge-neutral layers having the composition $[Mg(OH)_2]$ (Oswald and Asper 1977). When a fraction, *x*, of the Mg^{2+} ions is isomorphously substituted by trivalent ions, M'(III) (M' = Al, Cr, Fe), the hydroxide layers acquire a positive charge with the composition, $[Mg_{1-x}M'(III)_x(OH)_2]^{x+}$. Anions, A^{n-}, are incorporated in the interlayer region for charge neutrality, resulting in the formation of LDHs. The interlayer distance in LDHs depends on the nature, size and orientation of the intercalated anion, A^{n-}. It can vary from 7·6 Å for carbonates to as high as 47 Å for the vertical end-to-end bilayer arrangement of dodecylsulphate anions (Newman and Jones 1998). Many divalent ions such as Ca, Co, Ni, Cu and Zn can take the place of Mg^{2+} (Carrado *et al* 1988) leading to a large family of compounds.

LDHs are of interest as they show many useful properties such as anionic mobility (Oesten and Böhm 1993), anion exchange (Newman and Jones 1998; Khan and O'Hare 2002), sorption (Miyata and Hirose 1978) and surface basicity (Constantino and Pinnavaia 1995), by virtue of which they are used as sensors, catalysts, electrodes (Kamath *et al* 1994) and as precursors to nanoparticulate oxides (Uzunova *et al* 1997). There is, therefore, a tremendous interest in the synthesis of these materials.

Metal hydroxides are usually prepared by the addition of strong alkali to an appropriate metal salt solution according to the reaction

$$M_nA_m + n \times m\, NaOH \rightarrow nM(OH)_m + mNa_nA. \quad (1)$$

By extension, LDHs can be obtained by the coprecipitation from an appropriate mixed metal salt solution as

$$(1-x)MA_2 + xM'A_3 + 2NaOH + mH_2O \rightarrow$$
$$[M_{1-x}M'_x(OH)_2](A_x) \cdot mH_2O + 2NaA. \quad (2)$$
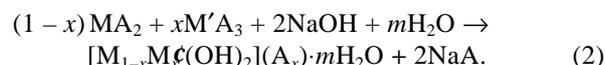
A coprecipitation reaction can only succeed if the phases being coprecipitated have comparable solubility products. However, in the present instance, solubility products of the divalent hydroxides (10^{-10}–10^{-16}) are several orders of magnitude higher than those of the trivalent metal hydroxides (10^{-31}–10^{-38}) (Dobos 1975). Consequently addition of a strong alkali to a mixed metal salt solution is expected to lead to serial precipitation of the trivalent metal hydroxide followed by the divalent metal hydroxide rather than to the formation of LDH.

However, the outcome of a precipitation reaction is affected by a number of factors (Grosso *et al* 1992), chief among them, being the pH at precipitation. This can be controlled by varying the sequence of addition of the reactants. By adding alkali to the metal salt solution, precipitation can be carried out at a low pH. By adding the salt solution to an excess of strong alkali, precipitation can be carried out at a constant high pH. Reichle (1986) suggested that by using the latter technique, the solubility products of both the divalent as well as the trivalent metal hydroxides could be simultaneously exceeded facilitating their coprecipitation. This method is now widely used and a very large number of diverse LDHs such as those containing Sc^{3+} (Rousselot *et al* 2002), V^{3+} (Rives *et al* 1993), Ga^{3+} (Rebours *et al* 1994) and In^{3+} (Aramendía *et al* 1999) have been pre-

*Author for correspondence

pared.

Despite this general understanding, Boclair and coworkers (Boclair and Braterman 1998, 1999; Boclair *et al* 1999) in a series of papers, reported the formation of LDHs in pH metric titrations, involving the slow addition of NaOH to a mixed metal ($M^{2+} + M'^{3+}$) salt solution. Two pH plateaus were observed, the first corresponding to the precipitation of the trivalent hydroxide, '$M'(OH)_3$', followed by the second, which was attributed to LDH formation. By establishing equilibrium after each stage of alkali addition, Boclair and Braterman (1999) estimated the nominal solubility products and the formation constants of a large number of LDHs. These include the LDH of Zn with Fe, which has not been reported to date and the LDHs of Mg and Ni with Cr (Boclair *et al* 1999) which are known to form only after prolonged hydrothermal treatment (Kooli *et al* 1995). Although the authors provide a table of *d*-spacings, no X-ray diffraction patterns have been provided, making it difficult to gauge the purity and crystallinity of the products obtained from the pH metric titrations.

The motivation for the present investigation is three-fold: (i) to obtain solid state evidence for the formation of LDH during pH metric titrations by powder X-ray diffraction studies, (ii) to determine the mechanism by which the trivalent hydroxide, '$M'(OH)_3$' reacts with the divalent metal salt solution to yield the LDH and (iii) to determine if pH metric titrations do indeed lead to the formation of new LDHs that have not been reported so far.

2. Experimental

2.1 *pH metric titrations*

250 ml of mixed metal ($M^{2+} + M'^{3+}$) nitrate/chloride solution, 0·2 M in M^{2+}, 0·1 M in M'^{3+} and 1 M in NO_3^- or Cl^- ions, was titrated pH metrically (CD, India, pH meter, Alchemie gel filled electrode) against a 50% wt/vol NaOH solution with constant stirring. The NaOH solution was suitably diluted and standardized prior to each titration. The NO_3^-/Cl^- strength of 1 M was attained by addition of the required quantity of $NaNO_3/NaCl$ to the mixed metal nitrate solution. The NaOH addition was done in steps of 0·1 to 0·5 ml and the pH measured after the solution was allowed to equilibrate. The time required for the pH to achieve a constant value can be as high as 15 min. The pH profiles of the titrations showed two plateau regions, which we refer to as I pH and II pH. The values of I pH and II pH for all the systems investigated in this paper are given in table 1.

The unary metal nitrates/chlorides were also titrated in separate experiments as controls. The anion strength was maintained at 1 M in all cases, by the addition of $NaNO_3/NaCl$. The pH profiles of these titrations showed a single plateau, on account of the precipitation of the correspond-

ing unary hydroxides. The pH values of these plateaus are listed in table 2.

For solid state characterization, a small amount of the solid was removed from the reaction mixture when 92% of the stoichiometric requirement of NaOH had been dispensed (Boclair and Braterman 1999). At this point the pH of the reaction mixture was in the region of the second plateau. The titration was then continued up to a final pH of 12. The solid was then filtered and copiously washed, till the wash turned neutral. The solids obtained at both stages were analysed by powder X-ray diffraction (PXRD) and infrared spectroscopy.

2.2 *Aging experiments*

To test the hypothesis (Boclair and Braterman 1999) that LDH formation takes place by the reaction of solid '$M'(OH)_3$' with the divalent metal salt in solution, stoichiometric quantities of freshly precipitated '$Al(OH)_3$', '$Fe(OH)_3$' and '$Cr(OH)_3$' were aged in a solution, 0·2 M in the divalent metal ion and 1 M in $NaNO_3$ or NaCl. After '$M'(OH)_3$' was suspended in this solution, the pH of the suspension was raised to the value of the II pH for the corresponding system by the addition of NaOH. In separate experiments, the aging was also carried out at pH > 12. The aging was carried out under constant stirring for up to 6 days at the ambient temperature (26–28°C). The

Table 1. pH values of first and second plateaus in pH titration profiles of mixed metal ($M^{2+} + M'^{3+}$) salt systems.

M(II)–M(III)	I pH	II pH
Mg–Al–Cl	3·6	7·5
Ni–Al–NO_3	3·6	6·3
Zn–Al–NO_3	3·65	~ 5·9
Mg–Fe–Cl	1·86	9·2
Ni–Fe–Cl	1·85	7·2
Zn–Fe–NO_3	1·85	6·0
Ni–Cr–Cl	3·4*	–

*This system shows only one plateau.

Table 2. pH values of the plateaus observed during pH metric titrations of unary metal salt solutions with NaOH and the corresponding pK_{sp} values.

Hydroxide	Plateau (pH)	pK_{sp} (expt)	pK_{sp} (literature value)
$Al(OH)_3$	3·7	31·9	32·72
$Cr(OH)_3$	3·6	31·9	30·17
$Fe(OH)_3$	1·9	37·3	37·42
$Mg(OH)_2$	9·2	10·3	11·26
$Ni(OH)_2$	7·2	14·3	13·79
$Zn(OH)_2$	5·9	16·9	16·69

solids obtained in both experiments were analysed by PXRD and infrared spectroscopy. 'Al(OH)$_3$', 'Fe(OH)$_3$' and 'Cr(OH)$_3$' were obtained by ammonia precipitation from the corresponding salt solutions. The resulting gelatinous precipitates were washed copiously with water to remove excess ammonia. The slurries were then used as such without drying.

All powder X-ray diffraction patterns were recorded using a JEOL Model JDX8P powder X-ray diffractometer (Co Ka source, l = 1·79 Å). The PXRD patterns were indexed on hexagonal cells (see table 3). Infrared spectra were obtained using a Nicolet Model Impact 400D FTIR spectrometer (KBr pellets, 4 cm^{-1} resolution).

3. Results and discussion

Titrations of unary metal salt solutions exhibit a single pH plateau corresponding to the precipitation of the corresponding hydroxide according to reaction (1). Expectedly the trivalent metals precipitate at a much lower pH than the divalent metals (table 2). The solubility products (pK_{sp}) calculated by the method of Boclair and Braterman (1999) from the pH values match well with those reported in the literature (Dobos 1975) (table 2). PXRD patterns showed all trivalent 'hydroxides' investigated here to be X-ray amorphous. This is not surprising in the case of Cr^{3+} and Fe^{3+}, since these are known to form hydrous oxide gels of type, M$_2$O$_3$·nH$_2$O. However, for convenience, these will be referred to as 'M′(OH)$_3$'. Al(OH)$_3$ is known to crystallize in two polymorphic modifications, bayerite and gibbsite (Wells 1979), but under conditions employed here only X-ray amorphous products were obtained.

PXRD investigations showed that the solid obtained from a Mg(NO$_3$)$_2$ solution was Mg(OH)$_2$ (Radha *et al* 2003), from Ni(NO$_3$)$_2$ it was b-Ni(OH)$_2$ (Ramesh *et al* 2003) and from Zn(NO$_3$)$_2$ it was Zn$_5$(OH)$_8$(NO$_3$)$_2$·2H$_2$O (this work).

Titrations of mixed metal (M^{2+} + M′$^{3+}$) salt solutions yielded a pH profile with two plateaus. In all cases the I pH value coincided exactly with the pH at which the corres-

ponding trivalent hydroxide precipitates showing that the first plateau is due to the precipitation of 'M′(OH)$_3$'. These observations are consistent with those made by Boclair and Braterman (1999). However, in contrast with the claims of Boclair and Braterman (1999), the II pH value is not always less than the pH at which the corresponding divalent hydroxide precipitates. The results are therefore discussed case by case.

3.1 *M(II)–Al(III) (M = Mg, Ni) systems*

Figure 1 compares the pH profile of the titration of a mixed metal (Mg + Al) chloride solution with the profiles of the titrations of the individual metal chlorides. The II pH value is 1·7 units less than the Mg(OH)$_2$ precipitation pH showing that the solid precipitated at this plateau is not Mg(OH)$_2$. PXRD pattern of the solid isolated from the reaction mixture at this stage reveals the formation of LDH (a = 3·04 Å; c = 23·19 Å) (figure 2a), which is characterized by the presence of a low angle reflection at 7·73 Å followed by another at 3·84 Å. Mg(OH)$_2$ on the other hand has a basal spacing of only 4·77 Å (a = 3·147 Å; c = 4·769 Å) (PDF: 7-239) (Smith 1967). Braterman and Boclair (1999) have suggested that LDH formation at the II pH value takes place due to a reaction between solid Al(OH)$_3$ and dissolved MgCl$_2$. To verify this hypothesis, freshly precipitated Al(OH)$_3$ was aged in a solution of MgCl$_2$ at a pH equal to the II pH value. Prolonged aging failed to yield LDH (figure 2c), showing that the second plateau observed during the titration is not due to LDH formation. However, aging Al(OH)$_3$ at pH > 12, yielded the LDH (figure 2b).

Similar results were found in the Ni–Al system as well (data not shown). Titration yielded the Ni–Al LDH. Aging solid Al(OH)$_3$ in a nickel nitrate solution at the II pH value (6·3) did not lead to LDH formation, while the aging experi-

Table 3. Cell parameters of LDHs obtained by aging as well as pH metric titration.

		Cell parameters	
	Method	c (Å)	a (Å)
MgAlCl LDH	Aging at pH > 12	23·0	3·04
MgAlCl LDH	During titration	23·2	3·04
MgFeCl LDH	Aging at pH = 9·27	23·2	3·10
MgFeCl LDH	During titration	23·7	–
ZnAlCl LDH	Before completion of titration	26·6	3·06
ZnAlCl LDH	After completion of titration	22·9	3·06
ZnAlCl LDH	Aging at pH = 5·6	26·1	3·06
ZnAlCl LDH*	Aging at pH > 12	22·7	3·06

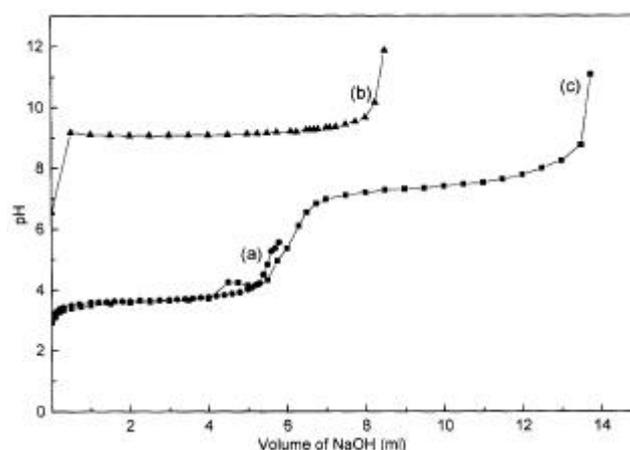*Peaks due to ZnO impurities were also present.

Figure 1. pH profiles of titrations of (a) an AlCl$_3$ solution, (b) a MgCl$_2$ solution compared with that of the (c) mixed metal (Mg + Al) chloride solution with NaOH.

ment carried out at pH > 12 led to the formation of the Ni–Al LDH.

These observations throw open the following questions: (i) what is the second pH plateau due to? (ii) why is LDH formation observed during the titrations? (iii) why is LDH formation observed in aging experiments carried out at high (> 12) pH but not at the II pH value?

We offer the following explanation.

$Al(OH)_3$ is amphoteric and as the pH is raised much above the I pH value, it begins to redissolve according to the reaction

$$Al(OH)_3 + OH^- \Leftrightarrow AlO_2^- + 2H_2O. \qquad (3)$$
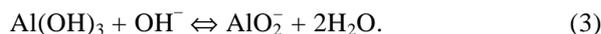
The rapid consumption of OH^- ions during this process is perhaps responsible for the II pH plateau. This occurs at a pH below that required for $Mg(OH)_2$ precipitation. LDH formation then takes place by the reaction between dissolved species as

$$AlO_2^- + 2H_2O + 2M^{2+} + 2OH^- + Cl^- \Leftrightarrow M_2Al(OH)_6Cl. \qquad (4)$$
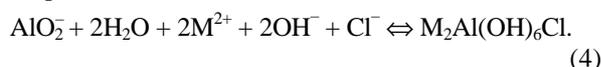
A continuous supply of OH^- ions is provided during titrations. LDH formation during titrations is therefore a result of kinetic rather than thermodynamic control. A similar situation exists during aging experiments carried out at high (> 12) pH, but not at low pH. Establishment of an equilibrium between the Mg–Al LDH and the products of its dissolution has been reported to take a time in excess of 100 days (Johnson and Glasser 2003). The method of Johnson and Glasser (2003) in our opinion is the best for the estimation of the solubility products of LDHs.

3.2 *M(II)–Fe(III) (M = Mg, Ni) systems*

Contrary to the claims of Boclair and Braterman (1999), the II pH value in all Fe containing systems was found to be exactly equal to the pH at precipitation of the unary divalent hydroxide (tables 1 and 2). We show in figure 3
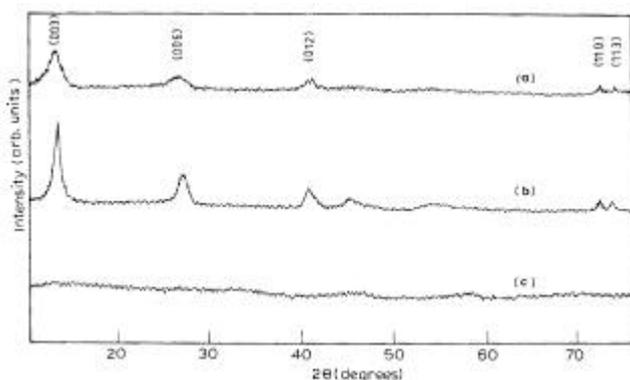
representative data obtained in the Mg–Fe titration. However, the solids obtained at the end of titration in the Mg–Fe and Ni–Fe cases exhibited the formation of LDHs. On the other hand, when 'Fe(OH)₃' slurries were aged in $MgCl_2$ and $NiCl_2$ solutions at their respective II pH values as well as at pH > 12, LDH formation was observed in the case of Mg (figure 4), but not in the case of Ni.

The fact that the II pH value coincides exactly with the pH at precipitation of the unary divalent hydroxide shows that the material precipitated at the second plateau is the unary divalent hydroxide and not LDH. The following questions arise: (i) why is LDH formation observed at the end of titrations? and (ii) why is LDH formation observed in aging experiments in the Mg–Fe system but not in the Ni–Fe system? We suggest that the LDH observed in the titration products is actually formed by coprecipitation induced by a steep increase in the local pH due to the addition of highly concentrated base during the titrations.
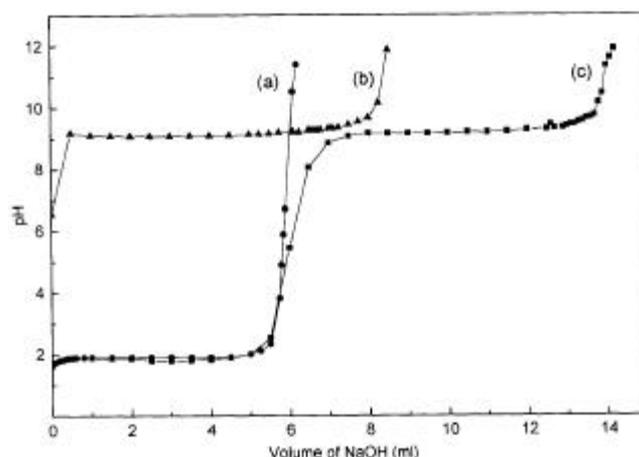
Figure 3. pH profiles of titration of (a) a FeCl₃ solution, (b) a MgCl₂ solution compared with that of the (c) mixed metal (Mg + Fe) chloride solution with NaOH.
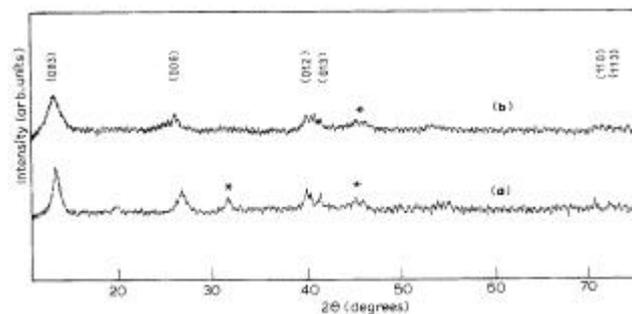
Figure 2. Powder X-ray diffraction pattern of (a) the phase precipitated during the titration of a mixed metal (Mg + Al) chloride solution compared with the products of an Al(OH)₃ gel aged in a MgCl₂ solution at (b) pH > 12 and (c) the II pH value.

Figure 4. Powder X-ray diffraction pattern of a Fe(OH)₃ gel aged in (a) a MgCl₂ solution at II pH value compared with (b) the phase precipitated during titration of mixed metal (Mg + Fe) chloride solution. Peaks marked by an asterisk are due to impurities.

These conditions are far from equilibrium. 'Fe(OH)$_3$' is also mildly amphoteric. The II pH value (9·2) is high enough to cause the dissolution of 'Fe(OH)$_3$' in the Mg–Fe system but not in the Ni–Fe system (7·2). Therefore, LDH formation is observed in aging experiments in the former by a mechanism similar to that in the Al containing systems but not in the latter.

3.3 *Ni(II)–Cr(III) LDH*

Mixed metal nitrate (Ni + Cr) titrations exhibit a single plateau suggesting a coprecipitation reaction as reported by Boclair *et al* (1999). However, the titrations as well as aging experiments carried out at the plateau pH (3·5) and high (> 12) pH, yield X-ray amorphous phases and LDH formation could not be established with certainty. Among the Cr(III) containing systems, except for the Zn–Cr LDH (Boehm *et al* 1977), other Cr(III) containing LDHs form only on hydrothermal treatment of the coprecipitated slurry (Kooli *et al* 1995).

3.4 *Zn(II)–M¢(III) (M¢= Al, Fe) systems*

In figure 5 are shown the pH profiles of the titrations in the Zn–Al system. This differs from the other Al containing systems in that the second plateau is poorly defined. The pH in this region rises gradually from the I pH value and the latter part of this plateau coincides with the pH at which Zn^{2+} precipitates. This behaviour is due to the proximity of the pHs at which the unary hydroxides precipitate. This situation promotes coprecipitation of the two metal hydroxides, by virtue of which the titrations yield the Zn–Al LDH. The LDHs isolated before and after completion of the titration exhibit different interlayer distances (figure 6) due to the exchange of intercalated carbonates
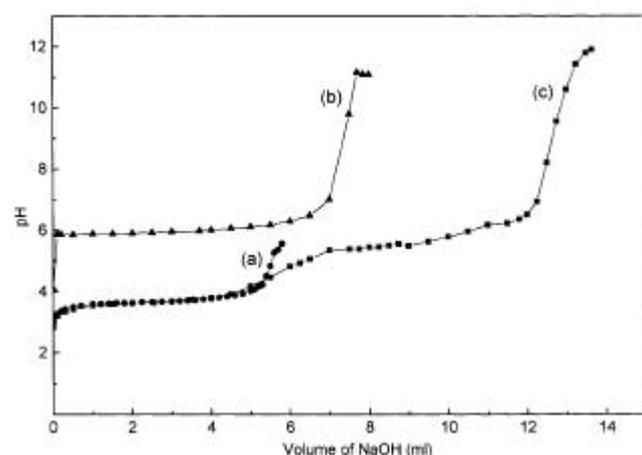
for nitrates at high pH. Aging experiments carried out at pH 5·6 yield the LDH while at pH 12, ZnO impurities are also observed in addition to LDH. When the aging experiment was carried out at pH > 12, only ZnO formation was observed (figure 7). This observation can be explained, if zinc hydroxide dehydration takes place before the dissolution of Al(OH)$_3$.

The Zn–Fe system is important, as no LDH of Zn with Fe has yet been reported. The behaviour of this system is similar to those of other Fe containing systems (figure 8) in that the II pH value is identical to the pH at precipitation of zinc hydroxide. We provide conclusive proof that no LDH formation is observed, as pH metric titrations of both the unary Zn salt as well as the mixed metal (Zn + Fe) nitrates led to the formation of the same product (figure 9) corresponding to Zn$_5$(OH)$_8$(NO$_3$)$_2$·2H$_2$O (PDF: 24-1460) (Smith 1967) at pH = 6. All diffraction maxima in both the patterns agree well with those reported for the zinc hydroxysalt with no evidence of Fe being incorporated in the lattice. The interlayer distance (7·81 Å) reported by Boclair and Braterman (1999) supposedly for the Zn–Fe LDH corresponds to Zn$_5$(OH)$_8$Cl$_2$·H$_2$O (PDF: 7-155) (Smith
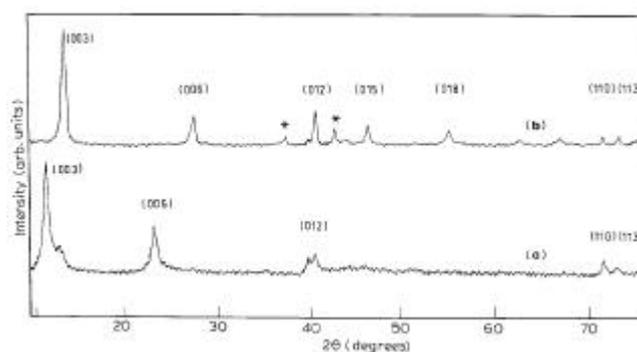
Figure 6. Powder X-ray diffraction patterns of the phases precipitated from a mixed metal (Zn + Al) nitrate solution (a) before and (b) after completion of titration. Peaks marked by an asterisk are due to impurities.
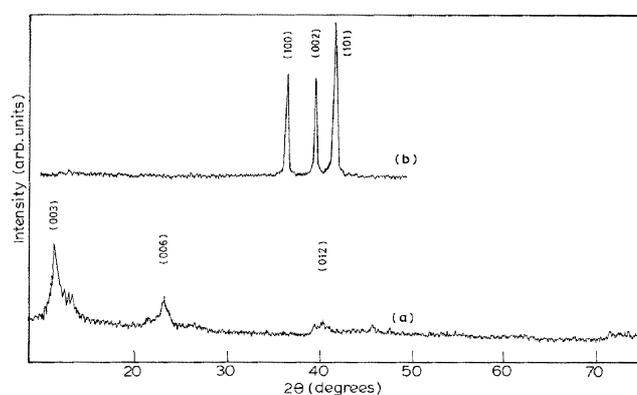
Figure 5. pH profiles of (a) an Al(NO$_3$)$_3$ solution, (b) a Zn(NO$_3$)$_2$ solution compared with that of the (c) mixed metal (Zn + Al) nitrate solution with NaOH.

Figure 7. Powder X-ray diffraction pattern of an Al(OH)$_3$ gel aged in Zn(NO$_3$)$_2$ solution at (a) the II pH value and (b) pH > 12.

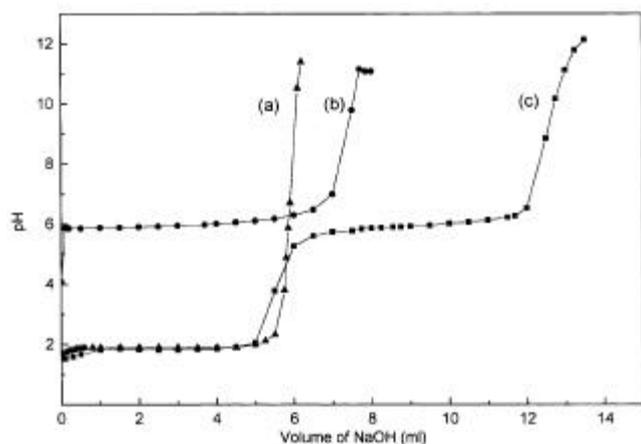**Figure 8.** pH profiles of (a) an $Fe(NO_3)_3$ solution, (b) a $Zn(NO_3)_2$ solution compared with that of the (c) mixed metal $(Zn + Fe)$ nitrate solution with NaOH.
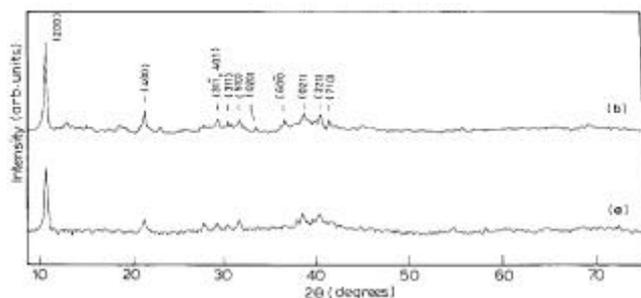

Figure 9. Powder X-ray diffraction pattern of the phase precipitated from (a) a mixed metal $(Zn + Fe)$ nitrate solution compared with (b) that precipitated from a zinc nitrate solution.

1967). At pH > 12, ZnO formation is observed.

4. Conclusions

When there is a large difference in the solubility products of the trivalent and divalent metal hydroxides, LDH formation proceeds by the dissolution of the trivalent hydroxide followed by the precipitation of LDH. When the solubility products of the two unary hydroxides are close as in the case of Zn–Al system, there is also the possibility of coprecipitation playing a major role in LDH formation. Caution must, however, be exercised in proposing common mechanisms for all LDHs as this family of compounds involves a diverse variety of constituents whose physical constants vary over many orders of magnitude.

Acknowledgements

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