

REGULAR ARTICLE

Nickel-zinc hydroxy salts with varying amounts of octahedral Zn²⁺: trends in stability and selectivity in anion exchange reaction

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Abstract. Nickel-zinc hydroxy acetates with varying amounts of octahedral zinc, Ni_(3-x)Zn_(2+x)(OH)₈(OAc)₂·mH₂O, with x varying from 0 to 2, have been synthesized. The crystallographic 'a' parameter increases linearly with octahedral zinc content in the series. While the thermal stability is almost the same for the entire series of compounds, the stability of the compound in the alkaline medium increases with a decrease in octahedral zinc content. The selectivity for chloride ion from a mixture of chloride and bromide ions increases linearly with an increase in octahedral zinc content.

Keywords. Anionic clay; hydroxy salt; anion exchange; selectivity.

1. Introduction

Selective ion exchange, a process by which a certain ion is preferentially removed while leaving the other ions in solution, has a great scope in the field of water treatment, catalysis and separation science.^{1–14} Anionic clays with positively charged layers and charge balancing anions in the interlayer are potential candidates for selective anion exchange. Anionic clays are broadly divided into two classes. In the first class of solids, called layered double hydroxides (LDH), the positive charge is brought about by isomorphous substitution of a part of the divalent metal ions of a brucite-like metal hydroxide by trivalent metal ions leading to the formula [M_(1-x)^{II}M_x^{III}(OH)₂]A_(x/n)⁽ⁿ⁻⁾·mH₂O.^{15,16} In the other class of anionic clays, the positive charge of the layer is brought about due to hydroxyl deficiencies or due to metal ions migrating to different sites. These are called layered hydroxy salts (LHS).¹⁷ Though anion exchange reactions of anionic clays are largely unselective, there are a few cases where the exchange has been found to be quite selective. The Li-Al-Cl LDH has been shown to be highly selective towards naphthalene dicarboxylate ions in solution.¹⁸ The LDH, Mg₂Al(OH)₆NO₃·2H₂O, has been shown to be selective towards arsenate ions

when treated with wastewater.¹⁹ Cobalt hydroxy salt, Co₃(OH)₄(NO₃)₂·2H₂O shows high selectivity for lower halides from a mixture of halide ions.²⁰

In an earlier report, we have shown that the zinc hydroxy salt, Zn₅(OH)₈(OAc)₂·2H₂O, has very high selectivity towards chloride ions when treated with a mixture of halide ions.²¹ This compound is made up of layers of edge-sharing octahedra of zinc coordinated to six oxygen atoms of hydroxyl groups. One-fourth of the octahedral sites are left vacant and the zinc ions occupy tetrahedral sites above and below the octahedral vacancy resulting in an overall positive charge for the layer. The layer composition of this hydroxy salt would be [Zn₃□Zn'₂(OH)₈]²⁺, where □ is the octahedral vacancy and Zn' are the ions in the tetrahedral sites.¹⁷

Though the zinc hydroxy salt shows high selectivity in halide exchange, it has limited operating pH range due to its amphoteric nature. A related compound, Ni₃Zn₂(OH)₈(OAc)₂·2H₂O, which has the same structure as the zinc hydroxy salt, with the zinc ions in the octahedral sites replaced by Ni²⁺, is quite stable in alkaline medium²² but shows poor selectivity in halide exchange. By varying the octahedral zinc content, it could be possible to optimize selectivity and stability

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in this system. Keeping this in mind, we have prepared a series of compounds of the formula $\text{Ni}_{(3-x)}\text{Zn}_{(2+x)}(\text{OH})_8(\text{OAc})_2 \cdot m\text{H}_2\text{O}$ with x varying from 0 to 2, and studied the evolution of stability and selectivity in anion exchange with the octahedral zinc content.

2. Experimental

2.1 Materials

Nickel acetate tetrahydrate, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (GR) was purchased from Aldrich Chemical Company while zinc acetate dihydrate, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (GR) and sodium hydroxide, NaOH, were purchased from Merck Chemical Company. All reagents were used as received without further purification.

2.2 Synthesis of hydroxy salts

A series of compounds with the formula $\text{Ni}_{(3-x)}\text{Zn}_{(2+x)}(\text{OH})_8(\text{OAc})_2 \cdot m\text{H}_2\text{O}$ with $x = 0-0.7$ were prepared using a modification of the hydrothermal method due to Nishizawa and Yuasa.²³ $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ were mixed in the required molar ratios in 50 mL of water such that the total metal ion concentration was 0.5 M. These solutions were heated at 130 °C for 4 h in Teflon lined stainless steel autoclaves. The solids obtained were centrifuged and washed several times with decarbonated water followed by acetone and dried in air at 65 °C. The samples are henceforth referred to as NiZnHA- x .

The nickel-free zinc hydroxy acetate (ZnHA) and nickel-zinc hydroxy acetates with high zinc content could not be prepared by the above method. ZnHA was prepared by adding 50 mL of 0.75 M NaOH to a 20 mL solution of 3.5 M zinc acetate.²⁴ The white solid obtained was washed several times with decarbonated water followed by acetone and dried in air at 65 °C. Similarly, $\text{Ni}_{(3-x)}\text{Zn}_{(2+x)}(\text{OH})_8(\text{OAc})_2 \cdot m\text{H}_2\text{O}$ with $x = 1.33$ and 2 were prepared by adding 0.75 M NaOH (50 mL) to a solution (20 mL) containing Ni^{2+} and Zn^{2+} in the required mole ratio such that the total metal ion concentration was 3.5 M. The pale green solids obtained were washed several times with decarbonated water followed by acetone and dried in air at 65 °C.

2.3 Stability of the hydroxy salts in alkaline medium

The stabilities of all the hydroxy salts in alkaline media were determined. In each case, ~200 mg of the hydroxy salt was dispersed in 50 mL of 1M NaOH and the mixture was stirred for 7 days. At the end of each day, aliquots of the solids were taken, washed with water several times followed by acetone and dried in air at 65 °C.

2.4 Competitive anion exchange with a mixture of chloride and bromide

Selectivity for chloride ion from a mixture of chloride and bromide ions was determined for all the hydroxy salts. In each case, about 200 mg of the hydroxy salt was dispersed in 50 mL of a solution containing 0.029 g of NaCl and 0.051 g of NaBr ($[\text{Cl}^-]/[\text{Br}^-] = 1$ and $[\text{Cl}^-] + [\text{Br}^-] = 1.5$ times the anion exchange capacity). The mixture was stirred for 48 h. The solids were separated by centrifugation, washed with water several times followed by acetone and dried in air at 65 °C.

2.5 Characterization

The solids were characterized by powder X-Ray diffraction (PXRD) using a PANalytical X'pert Pro diffractometer with $\text{Cu K}\alpha$ radiation, secondary graphite monochromator, with a scan rate of $2^\circ 2\theta$ /minute. Infrared spectra were recorded using a PerkinElmer Spectrum TWO Spectrometer in reflectance mode (ATR) with 4 cm^{-1} resolution. Thermal stability of the hydroxy salts was studied by thermogravimetric analysis using a Mettler Toledo Star^e SW 7.0, in airflow at a heating rate of 5 °C per min. The compositions of the solids were obtained by wet chemical methods. Both cation, as well as anion contents, were determined by ion chromatography using a Metrohm 861 Advanced Compact Ion Chromatograph. The solids were dissolved in minimum quantities of dilute HCl/dilute acetic acid and the solutions obtained were suitably diluted for this purpose. Cations (Ni^{2+} and Zn^{2+}) were estimated using Metrostep C2 250 cation column and anions (OAc^- , Cl^- and Br^-) were estimated using Metrostep A Supp5 250 anion column.

3. Results and Discussion

The compositions of the precursor solutions and the nominal compositions of the hydroxy salt samples obtained through wet chemical analysis are shown in Table 1. There is significant variation in the compositions of the chosen samples with the nickel content decreasing as we go from sample NiZnHA-0 to sample NiZnHA-2.0. During the hydrothermal synthesis, it was found that not all compositions were accessible and that the yield of the solid was found to decrease with decreasing nickel content. The centrifugate showed the presence of unreacted nickel and zinc in all the cases. The products were not formed for x in $\text{Ni}_{(3-x)}\text{Zn}_{(2+x)}(\text{OH})_8(\text{OAc})_2 \cdot m\text{H}_2\text{O}$ greater than 0.7. Therefore, NiZnHA-1.3, NiZnHA-2.0 and nickel-free ZnHA were prepared by coprecipitation/precipitation using NaOH.

The PXRD patterns of the samples, which are presented in Figure 1, are typical of layered materials

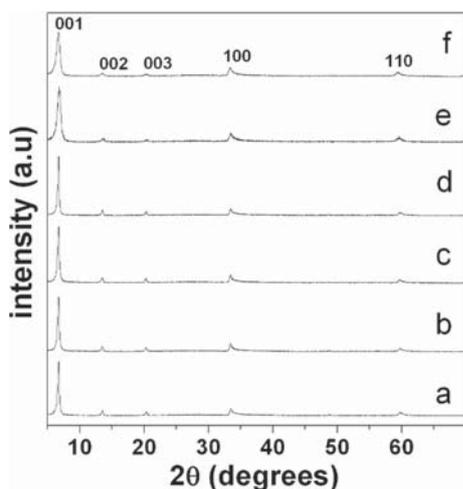
Table 1. The [Ni]/[Zn] ratios of the starting solutions and the products; the nominal compositions and the crystallographic ‘a’ parameters of the products.

Sample	[Ni]:[Zn] ratio in the precursor solution	[Ni]:[Zn] ratio in the product	Nominal composition of the product ^a	‘a’ Parameter (nm) ^b
NiZnHA-0	1.51	1.56	Ni ₃ Zn’ ₂ (OH) ₈ (OAc) ₂ ·mH ₂ O	0.3087
NiZnHA-0.3	0.93	1.21	Ni _{2.7} Zn _{0.3} Zn’ ₂ (OH) ₈ (OAc) ₂ ·mH ₂ O	0.3089
NiZnHA-0.5	0.57	1.03	Ni _{2.5} Zn _{0.5} Zn’ ₂ (OH) ₈ (OAc) ₂ ·mH ₂ O	0.3091
NiZnHA-0.7	0.32	0.87	Ni _{2.3} Zn _{0.7} Zn’ ₂ (OH) ₈ (OAc) ₂ ·mH ₂ O	0.3094
NiZnHA-1.3 ^c	0.50	0.49	Ni _{1.7} Zn _{1.3} Zn’ ₂ (OH) ₈ (OAc) ₂ ·mH ₂ O	0.3096
NiZnHA-2.0 ^c	0.25	0.25	Ni _{1.0} Zn _{2.0} Zn’ ₂ (OH) ₈ (OAc) ₂ ·mH ₂ O	0.3098
ZnHA ^c	–	0	Zn ₃ Zn’ ₂ (OH) ₈ (OAc) ₂ ·mH ₂ O	0.3103

^aThe nominal compositions were arrived at from Ni/Zn ratios. Zn and Zn’ refer to zinc ions in octahedral and tetrahedral sites respectively.

^bThe crystallographic ‘a’ parameter was calculated using d₁₁₀ and d₁₁₁.

^cNickel zinc hydroxy salts with high zinc content and nickel-free zinc hydroxy salt could not be prepared by the hydrothermal method. These were prepared by coprecipitation/precipitation using NaOH.

**Figure 1.** PXRD patterns of the nickel-zinc hydroxy salts: NiZnHA-0 (a), NiZnHA-0.3 (b), NiZnHA-0.5 (c), NiZnHA-0.7 (d), NiZnHA-1.3 (e) and NiZnHA-2.0 (f).

showing sharp symmetric reflections at a low angle and weak asymmetric reflections at a high angle. The system is indexed based on a pseudohexagonal cell and the patterns are comparable to that reported in earlier studies.²³ The interlayer spacing of 12.9 Å, calculated using the three 00 l reflections, confirms the incorporation of acetate anions in the interlayer region. The 100 peak located at $2\theta \sim 34^\circ$ shifts slightly to the right (Figure 2A) with decreasing nickel content. The ‘a’ parameter, calculated from 100 and 110 peaks, was seen to increase with a decrease in nickel content in accordance with Vegard’s law (Figure 2B). The IR spectra of the samples (Figure S1, Supplementary Information) confirmed the incorporation of the acetate ion into the interlayer presenting the symmetric

and antisymmetric bands at 1542 and 1383 cm^{-1} due to the C=O stretching vibrations of the acetate ions. The presence of a broad peak due to the OH group at 3470 cm^{-1} indicates that the acetate ion is not directly bonded to the tetrahedral zinc but is held in the interlayer by hydrogen bonding interactions. This is in agreement with the earlier studies on zinc hydroxy acetate.²¹

The thermogravimetry results of the samples with two different nickel contents, NiZnHA-0 and NiZnHA-0.7, are shown in Figure 3. While there is no drastic difference in the thermal stability of the compounds, the onset of thermal decomposition is shifted slightly to a higher temperature on increasing the nickel content. There are two major steps in the decomposition. The first loss (6.8% for NiZnHA-0 and 13.2% for NiZnHA-0.7) corresponds to the loss of adsorbed and interlayer water molecules and the second step, which is seen in the temperature range of 200 °C–300 °C (29.5% for NiZnHA-0 and 31% for NiZnHA-0.7), corresponds to the dehydroxylation and decomposition of the compound. The observed mass losses match with the values expected from the nominal formulas.

The data obtained on the alkali ageing studies are presented in Figure 4. The stability in alkaline media decreases with decreasing nickel content in the sample. The sample with all three octahedral zinc replaced by nickel (NiZnHA-0) remains stable even after 7 days. NiZnHA-0.3 is stable for one day. At the end of two days, it starts converting to ZnO and Ni(OH)₂ though the major phase is still the hydroxy salt with a reduced basal spacing due to exchange of interlayer acetate with carbonate. NiZnHA-0.5 and NiZnHA-0.7

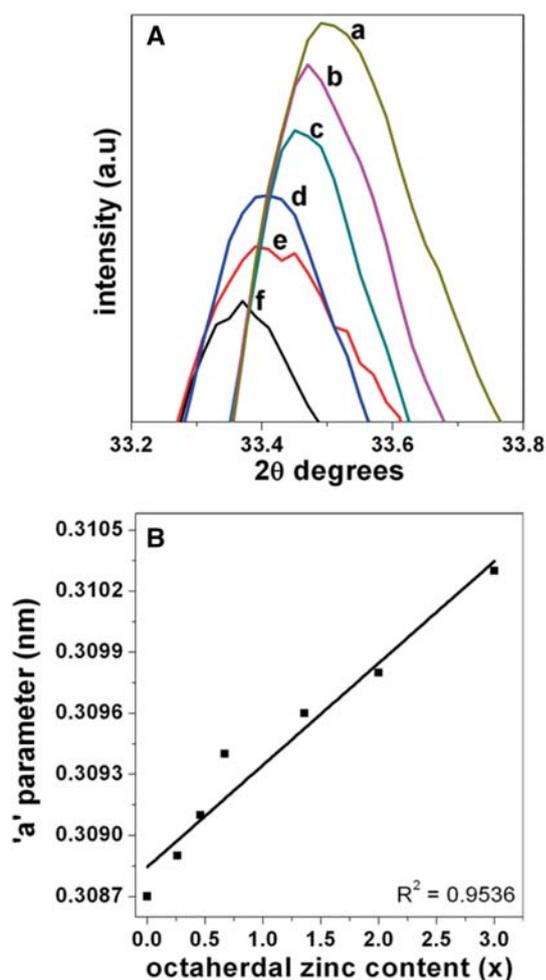


Figure 2. A: PXRD patterns of the nickel-zinc hydroxy salts recorded under slow scan rate and expanded in the region of 100 reflection: NiZnHA-0 (a), NiZnHA-0.3 (b), NiZnHA-0.5 (c), NiZnHA-0.7 (d), NiZnHA-1.3 (e), and NiZnHA-2.0 (f). B: Plot of 'a' parameter of the hydroxy salt against x , the octahedral zinc content. The data point corresponding to $x=3$ is from our earlier work.²¹

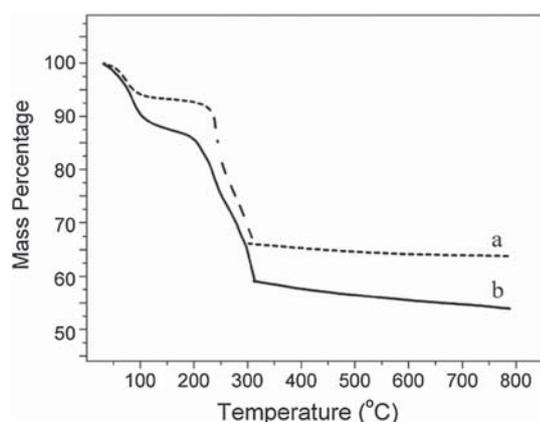


Figure 3. Thermogravimetry (TG) plots of the nickel-zinc hydroxy salts: NiZnHA-0 (a), and NiZnHA-0.7 (b).

are not stable as they convert to carbonate intercalated hydroxy salt within one day and completely convert to ZnO and Ni(OH)₂ within 7 days. Ni²⁺, whose hydroxide is stable in alkaline medium, prevents the hydroxy salt from dissolving in alkali and hence the stability in alkaline medium increases with an increase in the nickel content.

The PXRD patterns of the anion exchanged samples (Figure S2 a, b, Supplementary Information) indicate that the larger acetate ion has been replaced by the smaller halide ions. The hydroxy salt phase remains intact after the exchange. The PXRD pattern of the thermal decomposition product of a halide-exchanged sample (Figure S2 c, Supplementary Information), obtained by heating the halide-exchanged sample at 600 °C for 2 h, shows peaks due to NiO and ZnO suggesting that zinc is not leached out of NiZnHA samples during anion exchange.

There is a trend in selectivity for chloride ion in the competitive anion exchange reaction as shown in Table 2. NiZnHA-0 shows poor selectivity though it prefers chloride slightly over bromide. The solid becomes more selective towards chloride ions as the nickel content decreases, but the selectivity is nowhere compared to that of the parent compound. The selectivity increases linearly with an increase in octahedral zinc content (Figure 5). The observed trend could possibly be due to the small change in the 'a' parameter leading to an increase in the average metal-metal distance in the metal hydroxide layer. The increased metal-metal distance seems to increase the interaction of the metal hydroxide layer and chloride ion possibly through better H-bonding between the anion and the layer hydroxyl groups.

4. Conclusions

Compounds of the formula Ni_(3-x)Zn_(2+x)(OH)₈(OAc)₂·mH₂O with varying x could be synthesized by the hydrothermal and coprecipitation methods. While the stability in alkaline medium is seen to increase with increasing nickel content, the thermal stability does not change much with the change in nickel content. There is a trend in selectivity in anion exchange with the compound becoming more and more selective towards chloride ions in a mixture of chloride and bromide ions as the zinc content increases. While there seems to be a correlation between the average metal-metal distance and the preference for chloride, the mechanism of selectivity can be understood only through extensive studies with different anionic clays.

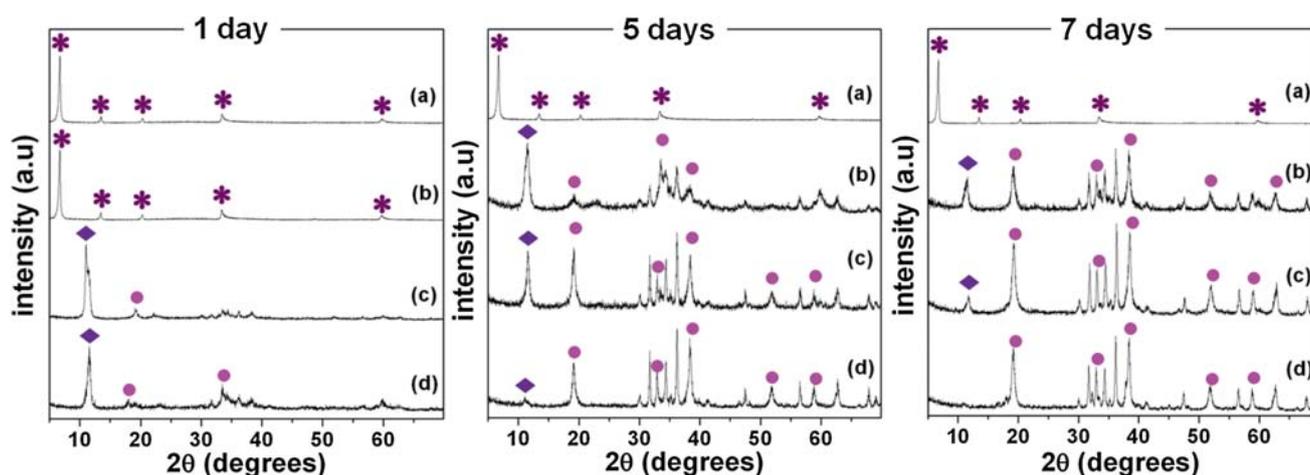


Figure 4. PXRD patterns of the products obtained on ageing the nickel-zinc hydroxy salts in alkali for different durations: NiZnHA-0 (a), NiZnHA-0.3 (b), NiZnHA-0.5 (c) and NiZnHA-0.7 (d). Peaks due to NiZnHA, its carbonate exchanged product and Ni(OH)₂ are indicated by *, ◆ and ● respectively.

Table 2. Selectivity of the hydroxy acetates for chloride from a mixture of chloride and bromide in competitive anion exchange reaction.

Sample	% Uptake of chloride	% Uptake of bromide
NiZnHA-0	59 ± 3	41 ± 2
NiZnHA-0.3	67 ± 2	33 ± 1
NiZnHA-0.5	71 ± 1	29 ± 4
NiZnHA-0.7	71 ± 2	30 ± 2
NiZnHA-1.3	82 ± 3	19 ± 2
NiZnHA-2.0	85 ± 2	15 ± 3

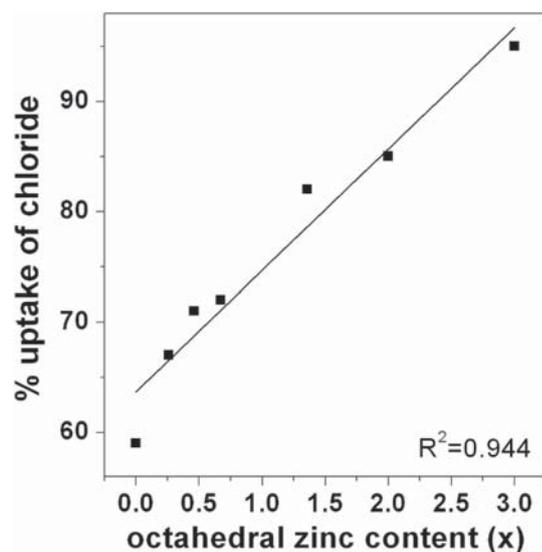


Figure 5. Plot of the percentage uptake of chloride ions from a mixture of chloride and bromide against x , the octahedral zinc content. The data point corresponding to $x=3$ is from our earlier work.²¹

Supplementary Information (SI)

Figures S1–S2 are available at www.ias.ac.in/chemsci.

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