Surface charging of layered double hydroxides during dynamic interactions of anions at the interfaces

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ABSTRACT

In this research, we investigated the effect of dynamic anion adsorption/exchange on the surface charging property of $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$ and $\text{Mg}_2\text{Al}-\text{CO}_3-\text{LDH}$ particles that show the average zeta potential of 41 and 34 mV in the as-prepared suspension, respectively. The addition of NaCl up to 3×10^{-3} M in the suspension does not obviously affect the zeta potential of both LDHs, which can be attributed to the less affinity of Cl^- to LDH. The introduction of Na_2CO_3 severely reduces the zeta potential at the CO_3^{2-} concentration higher than 1×10^{-4} M, and to the negative value in both LDH systems at ca. 2×10^{-3} M, which is presumably resulted from the exchange and the re-orientation of CO_3^{2-} in a tilt/vertical style on the surface. All four organic anions (dodecyl sulfate, folate, citrate and polyacrylate) also significantly affect the zeta potential of the LDH particles. At the lower concentrations of organic anionic groups ($< 1 \times 10^{-4}$ M), the zeta potential was slightly affected, i.e. limited exchange/adsorption. However, the concentration increasing to some point suddenly decreases and reverses the zeta potential of the LDH particles, which is presumably caused by the hydrophobic interactions that bind the hydrophobic hydrocarbon chains (especially in dodecyl sulfate) into the micelle-like bilayer bunches on the LDH surface. In addition, the effect of pH in 5.5–11.0 on the LDH particle surface charging is mainly reflected through the conversion of CO_3^{2-} to $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ when pH decreases from ca. 11 to 6, with limited contribution from protonation/deprotonation and exchange/adsorption.

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1. Introduction

Inorganic nanoparticles have been emerged as new non-viral delivery agents only in the recent decade, and there are many inorganic materials, such as calcium phosphate, gold, carbon materials, silicon oxide, iron oxide and layered double hydroxides (LDHs), being extensively investigated [1]. This is due to recognition of their versatile features suitable for cellular delivery, such as wide availability, rich surface functionality, good biocompatibility, potential capability of target delivery and sustained release [1]. In particular, LDH has been paid more attention as efficient delivery vehicles of drug, nucleotides/genes, biomedical and other functional molecules [2–4].

LDH, also known as hydrotalcite-like material, can be found in nature as minerals and readily synthesized in the laboratory, with majority adhering to the general formula $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{II} represents a divalent metal cation, M^{III} a trivalent metal cation and A^{n-} an anion. Struc-

turally, LDHs consist of cationic brucite-like layers and interlayer anions as well as water molecules. In the brucite-like layer $[\text{M}^{\text{II}}(\text{OH})_2]$, the partial substitution of M^{II} by M^{III} leads to a positive charge $([\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+})$, which is neutralized by the interlayer exchangeable anion $[(\text{A}^{n-})_{x/n}]$ while various amounts of water ($m\text{H}_2\text{O}$) are hydrogen bonded to the hydroxide layers and/or to the interlayer anions [5,6], forming the 3-D layered structure.

LDH particles prepared in the laboratory are normally hexagonal platelets, with the lateral sizes varying from 50 to 1000 nm and the aspect ratio in 5–10, while they are severely agglomerated into aggregates with the sizes up to 10 μm [7,8]. Recently, we developed a reliable method with which the LDH platelet dimension can be well controlled in 50–300 nm and these platelets can be homogeneously dispersed in the aqueous suspension [8]. Therefore, if the LDH platelet dimension is controlled under 150–200 nm, the cellular delivery of such LDH platelets should be efficient [9]. However, when we further carried out the delivery of supercoiled pEF-eGFP plasmid (ca. 6.1 kbp) to various cell lines using these LDH particles, we noted that the delivery efficiency was rather low in comparison with the polymeric delivery vehicle [10]. Many other papers reported the successful delivery of various gene segments

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[3,11–13], but the efficiency was much lower than the commercial polymeric agents [1,3,10,13]. The low delivery efficiency, in our belief, is due to aggregation of LDH–DNA hybrid particles into large aggregates during preparing the LDH–DNA nanohybrid suspension and mixing it to the culture medium.

It is well known that dispersion and aggregation of any particles in the suspension are related to their zeta potential [14]. Because inorgano-LDH particles normally have a zeta potential of 30–50 mV, they can be well dispersed in the suspension with the suitable methods, such as hydrothermal treatment [15]. However, this high positive zeta potential is reduced when the particles are interacting with gene segments, or with organic/inorganic salts in solution, which could finally lead to agglomeration and sedimentation. Therefore, in this research, we dynamically investigated the surface charging of fully dispersed LDH particles in aqueous suspension when the organic/inorganic anions at various concentrations are interacting on the particle surface in order that we understand the surface charging and agglomeration of LDH particles in the salt solution, such as phosphate buffer saline solution.

2. Experimental

2.1. Preparation of LDH materials

Mg₂Al–Cl–LDH and Mg₂Al–CO₃–LDH particle suspensions were prepared with a quick precipitation and subsequent hydrothermal treatment [8,15]. In brief, 3.0 mmol of MgCl₂·6H₂O (>98%, Aldrich) and 1.0 mmol of AlCl₃·6H₂O (>98%, Aldrich) were dissolved in 10 mL deionized water. This salt solution was then rapidly added to a basic solution (40 mL) containing 6.0 mmol of NaOH (>97%, Ajax Finechem) within 5 s to generate the precipitate of Mg₂Al–Cl–LDH. After stirring for 10 min in N₂ stream at room temperature, the precipitate was collected via centrifugation and further washed twice. Henceforth, the washed precipitate was manually dispersed in 40 mL of deionized water and placed in a 45 mL autoclave with Teflon linen, followed by hydrothermal treatment at 100 °C in an oven for 16 h to give the suspension of Mg₂Al–Cl–LDH particles (regarded as ‘salt-free’ suspension).

Similarly, 2.0 mmol of MgCl₂·6H₂O and 1.0 mmol of AlCl₃·6H₂O were dissolved in 10 mL deionized water, which was then rapidly added to a basic solution (40 mL) containing 6.0 mmol of NaOH and 0.6 mmol of Na₂CO₃ (>99%, Ajax Finechem) within 5 s to generate the precipitate of Mg₂Al–CO₃–LDH and stirred for 10 min at room temperature. The stirred mixture was post-treated in the same way as above to generate the suspension of Mg₂Al–CO₃–LDH particles.

2.2. Materials characterization

Mg₂Al–Cl–LDH and Mg₂Al–CO₃–LDH materials were identified by X-ray powder diffraction (XRD), using a Bruker D8 Advance Research X-ray diffractometer with copper K_α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 1.2°/min over a 2θ range of 8°–65°. The LDH samples were mounted on glass slides in the thin film form by dropping a few drops of the as-prepared LDH particle suspension. The instrument was calibrated with the crystalline silicon and the basal spacing was determined from the characteristic diffraction peaks. Fourier transform infrared (FTIR) spectra were acquired over the range of 4000–400 cm^{−1} with 40 scans at a resolution of 4.0 cm^{−1} on a Nicolet 6700 FTIR by measuring the KBr pellet containing 1–2 wt% of the LDH sample.

Photon correlation spectroscopy (PCS, Nanosizer Nano ZS, Malvern Instruments) was used to analyze the particle size distribution of the LDH suspensions from 0.6 to 6000 nm at 25 °C, in which the peak position was automatically calculated. The water refractive index (RI) of 1.33 and the water viscosity of 0.8872 cP

were employed while the RI of LDH materials was arbitrarily assigned 1.55.

The transmission electron microscopic (TEM) images were recorded on a JEOL JSM-2010 transmission electron microscope (TEM) at an acceleration voltage of 200 kV. For TEM imaging, a droplet of the diluted as-prepared LDH particle suspension (1:10) was dropped on a copper grid coated with the holey carbon film.

2.3. Zeta potential monitoring during titrations

Zeta potentials of the two diluted LDH suspensions were also measured using the Zetasizer Nano ZS (Malvern Instruments) with the water RI of 1.33, the water dielectric constant of 78.55 and the water viscosity of 0.8872 cP. In order to dynamically monitor the change of the zeta potential when an organic/inorganic salt or acid/base solution was continuously mixed with the LDH suspension, the measurement was performed using the MPT-2 Autotitrator associated to Zetasizer Nano ZS where the titration system was well sealed. In the first step, each LDH suspension of 1.0 mL was diluted with 9.0 mL of deionized water in a 25 mL sample container which was then attached to the MPT-2 Autotitrator. The diluted LDH suspension was kept at 25 °C and started to circulate into the zeta cell. The zeta potential was monitored and became stabilized after circulation for 3–5 min. After stabilization, the zeta potential was read by accumulating 30 times, which was regarded as the zeta potential of the as-prepared LDH particles.

In the next step, the diluted LDH suspension was injected with dilute NaOH solution (0.01 M) to adjust pH of the LDH suspension (ca. 9.0) to ca. 11.0 via the autotitration set-up. The zeta potential and the exact pH were read after the reading was stabilized. To monitor the zeta potential changing with pH, the dilute HCl (0.01 M) was automatically injected to the LDH suspension to change pH to a pre-designed value in the range from 11.0 to 5.5. After injection, the suspension was circulated, and zeta potential was measured only after the zeta potential reading became stable. Then the injection of dilute HCl solution was repeated to the next pH until to 5.5. The reverse autotitration from pH 5.5 to 11.0 was continued with injecting dilute NaOH solution in the similar way, with recording the zeta potential at each pH.

Alternatively, an inorganic/organic salt solution was injected to the diluted LDH suspension to investigate the dynamic exchange/adsorption of the inorganic/organic anion on the LDH particle surface at 25 °C through monitoring the zeta potential change. For example, dilute NaCl (0.01 M) or Na₂CO₃ (0.01 M) solution was added to the LDH suspension with [Cl[−]] or [CO₃^{2−}] varying from 1.0×10^{-5} to 3.0×10^{-3} M. At each pre-designed concentration point, the LDH suspension was circulated until the zeta potential reading was stable. In comparison, some organic anions were selected, including dodecyl sulfate (singly charged), folate (doubly charge), citrate (triply charged) and poly(acrylate) (multiply charged, MW = ~10,000). Their sodium salt solutions were made and auto-titrated to increase the anionic group (functionality: COO[−] or R–OSO₃[−]) concentration from 1.0 – 3.0×10^{-5} to 3.0 – 9.0×10^{-3} M, while the zeta potential at each point was monitored.

3. Results

3.1. Physicochemical features of LDH particles

Two as-prepared LDH suspensions look homogeneous and very transparent, with the LDH crystallite particles being well suspended in solution. As shown in Fig. 1, there is one distribution band for each LDH suspension. For instance, Mg₂Al–Cl–LDH particles have the hydrodynamic diameters exclusively in 30–250 nm

Fig. 1. Particle size distribution of the as-prepared $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ and $\text{Mg}_2\text{Al-Cl-LDH}$ suspensions.

(A)

(B)

Fig. 2. TEM images of (A) $\text{Mg}_2\text{Al-Cl-LDH}$ and (B) $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ particles.

(A)

(B)

Fig. 3. XRD patterns (A) and FTIR spectra (B) of $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ and $\text{Mg}_2\text{Al-Cl-LDH}$ materials.

with the peak at 115 nm, while $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ particles are distributed around ca. 80 nm in the size range of 25–180 nm. The hydrodynamic diameters are relatively similar to the lateral dimension of LDH platelets measured in TEM images (Fig. 2). Fig. 2 shows that both LDH particles are hexagonally sheet-like. The lateral diameters of $\text{Mg}_2\text{Al-Cl-LDH}$ platelets are mostly 80–200 nm and those of $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ platelets are 30–100 nm. It seems that $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ platelets are relatively thicker than $\text{Mg}_2\text{Al-Cl-LDH}$, due to the stronger affinity of CO_3^{2-} to LDH that causes more hydroxide layers to stack on top of one another [16].

The XRD patterns of LDH materials deposited on the glass plates in the thin film form exhibit the typical layered features and demonstrate a good crystallinity, as shown in Fig. 3A. The d-spacing is 0.772 nm for $\text{Mg}_2\text{Al-Cl-LDH}$ and 0.764 nm for $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$, respectively, quite similar to those reported elsewhere [6]. Very interestingly, only basal diffractions [(003), (006) and (009), etc.] are observable in the patterns while other non-

Fig. 4. Zeta potential distribution of $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ and $\text{Mg}_2\text{Al-Cl-LDH}$ particles.

basal characteristic diffractions, such as (015), (018), (110) and (113), are not. This indicates that the LDH platelets are flatly laid on the glass plate after drying, as also seen in TEM images where LDH platelets are almost all flatly laid on the sample support. The full width at the half maximum (FWHM) of peaks (003) and (006) suggests that the thickness of both LDH platelets is ca. 15 nm on average, as estimated by using the Debye–Scherrer equation without any correction [17]. Thus the aspect ratio is ca. 8 and 5 for $\text{Mg}_2\text{Al-Cl-LDH}$ and $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ platelets, respectively. In addition, elemental analysis gives the atomic ratio $[\text{Mg}]/[\text{Al}]$ of ~ 1.9 , slightly less than the designed value (2.0), attributed to more Mg^{2+} leaching than Al^{3+} from the hydroxide layers during hydrothermal treatment [18]. The leaching of more Mg^{2+} may also lead to formation of traces of gibbsite, as marked with # in Fig. 3A. Thus, the nominal chemical formula of $\text{Mg}_2\text{Al-Cl-LDH}$ and $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ are approximately $\text{Mg}_{1.9}\text{Al}(\text{OH})_{5.8}\text{Cl}\cdot m\text{H}_2\text{O}$ and $\text{Mg}_{1.9}\text{Al}(\text{OH})_{5.8}(\text{CO}_3)_{0.5}\cdot n\text{H}_2\text{O}$ ($m, n = 2\text{--}4$ depending the drying conditions). Based on the metal contents, the LDH particle concentration is approximately 0.4 wt% in both as-prepared suspensions.

FTIR spectra in Fig. 3B are characteristic of $\text{Mg}_2\text{Al-LDH}$ materials. For example, $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ is featured in the FTIR spectrum with a broad band at 3420 cm^{-1} (ν_{OH}), a shoulder at 3020 cm^{-1} (ν_{OH} for O–H that interacts with CO_3^{2-} through H-bond), a peak at 1605 cm^{-1} ($\delta_{\text{H}_2\text{O}}$), a strong peak at 1357 cm^{-1} [$\nu(\text{CO}_3^{2-})$] and bands at 785 , 680 and 447 cm^{-1} (M–O vibrations and M–O–H bending). $\text{Mg}_2\text{Al-Cl-LDH}$ shows the similar IR spectrum, but without the shoulder at 3020 cm^{-1} , with a rather weak peak at 1361 cm^{-1} (due to CO_3^{2-} contamination from CO_2 in air) and the band at 785 cm^{-1} shifting to 677 cm^{-1} [6,19–21]. In particular, the sharp peak at 447 cm^{-1} is the definite evidence of $\text{Mg}_2\text{Al-LDHs}$ [19,21].

3.2. Zeta potential of as-prepared LDH particles

Zeta potentials of both types of LDH particles in the suspension are positive, and distributed from 20 to 65 mV ($\text{Mg}_2\text{Al-Cl-LDH}$) and from 10 to 55 mV ($\text{Mg}_2\text{Al-CO}_3\text{-LDH}$), as shown in Fig. 4. The distribution of the zeta potentials indicates that the LDH surface is heterogeneous in terms of the surface charge. For instance, the

Fig. 5. Plots of the zeta potential of $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ (open triangle: forth; open circle: back) and $\text{Mg}_2\text{Al-Cl-LDH}$ (block square: forth; block diamond: back) particles vs the solution pH.

charge density may be different on the c-plane and a/b-plane as well as on the edges and basal regions. The average zeta potential given by the instrument is 41 and 34 mV for $\text{Mg}_2\text{Al-Cl-LDH}$ and $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$, respectively. The average zeta potential was reported hereafter for the convenience of comparison.

The positive zeta potential of LDH particles is in principle attributed to the structural positive charge and the electric double layer on the LDH surface. Although the interior structural charges in the hydroxide layers are fully screened by the interlayer anions, the surface structural charges are not fully balanced by the adsorbed surface anions because of the existence of the electric double layer, i.e. Stern layer and diffusion layer. Since the surface adsorbed anions thermally vibrate and temporarily leave the Stern layer, there are always some anions statistically in the diffusion layer, and thus the LDH particle associated with the Stern layer is positively charged. The simulation reveals that ca. 4% of the surface structural charges are not balanced by Cl^- in $\text{Zn}_2\text{Cr-Cl-LDH}$ [22]. In general, since CO_3^{2-} is more strongly adsorbed on the surface than Cl^- , more surface CO_3^{2-} ions are kept in the Stern layer, i.e. less CO_3^{2-} in the diffusion layer, thus $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ particles show a smaller zeta potential (30–35 mV) than $\text{Mg}_2\text{Al-Cl-LDH}$ (40–50 mV), as reported [15]. In addition, the zeta potential of LDH particles in the suspension is little changed when the LDH concentration is varied in 0.1–4.0 wt% [15,23]. Our observation was that there was 3–4 mV difference (i.e. similar to the measurement error) when 0.4 wt% LDH suspension was diluted by 10 times in the titration experiments.

3.3. pH effect on the zeta potential

As shown in Fig. 5, when pH of the LDH suspension is decreased from ca. 11 to 5.5, the zeta potential of $\text{Mg}_2\text{Al-Cl-LDH}$ particles is only slightly increased from ca. 38 to 44 mV. When the back titration with dilute NaOH solution increases pH from 5.5 to 11.0, the zeta potential of $\text{Mg}_2\text{Al-Cl-LDH}$ particles is slightly smaller at each corresponding pH (Fig. 5). The irreversibility of the zeta potential in the back and forth titration is expected to be mainly due to the ionic strength effect as well as the possible dissolution at $\text{pH} < 6$. For $\text{Mg}_2\text{Al-LDH}$ system, the zeta potential reading became not stable when pH was tried to reach below 5 or above 12, which is presumably caused by the dissolution of LDH

at pH below 5 [24] or the Al^{3+} leaching from the layers at pH above 12.

On the other hand, the zeta potential of $\text{Mg}_2\text{Al}-\text{CO}_3$ -LDH particles is increased from 30 to 45 mV when pH is changed from 11 to 6.0, more significantly at pH below 8. Such a change trend with pH was also reported by Lagaly et al. for $\text{MgAl}-(\text{NO}_3, \text{CO}_3, \text{Cl})$ -LDH particles [25]. Apart from the effect of the ionic strength and dissolution at pH < 6, increasing the zeta potential of $\text{Mg}_2\text{Al}-\text{CO}_3$ -LDH is probably caused by the following consequent reactions during the HCl addition:

In solution, there is an equal amount of CO_3^{2-} and HCO_3^- at pH ≈ 10.2 . As pH is lowered to 7–8, more than 99% CO_3^{2-} anions on the surface are theoretically transferred to HCO_3^- . Since the in situ produced HCO_3^- as well as the added Cl^- have a less affinity for LDH than CO_3^{2-} , thus these LDH particles exhibit a higher zeta potential at a lower pH. Moreover, half HCO_3^- are changed to H_2CO_3 at pH ≈ 6.4 that has a much less affinity for LDH and is readily replaced. Also note that the zeta potential is higher at each corresponding pH during the back titration of the $\text{Mg}_2\text{Al}-\text{CO}_3$ -LDH suspension with NaOH from pH 6 to 11 (open circle in Fig. 5). This is because the surface CO_3^{2-} anions were already transferred to H_2CO_3 during the HCl titration to pH 6 and replaced by Cl^- , and thus the zeta potential became higher during the back titration with NaOH.

During the dynamic titration, a few processes, i.e. protonation (Eq. (2)), deprotonation (Eq. (3)) and anion exchanges (Eqs. (3) and (4)) [22,26], simultaneously take place and affect the zeta potential of Mg_2Al -LDH particles:

Based on the relative small variation of the zeta potentials during the titration with dilute HCl, the contribution of protonation (Eq. (2)) and deprotonation (Eq. (3)) is little significant and can be ignored when pH is 7–10. When pH < 7, the surface hydroxide layer starts protonation (Eq. (2)) and dissolution [24]. This will increase the zeta potential of LDH particles [22], particularly for Mg_2Al -LDH system, as observed in this research. When pH > 10, deprotonation (Eq. (3)) takes place [22,26] and results in a smaller zeta potential. In practice, we observed the decrease of the zeta potential by ca. 4 mV when pH of LDH suspension was adjusted from ca. 9.0 (diluted LDH suspension) to ca. 11.0. This decrease is not significant but still detectable. In addition, the modeling results reveal that deprotonation of $\text{ZnCr}-\text{Cl}$ -LDH particles would be significant at pH > 10 [22].

Since pH of LDH suspensions is varied only in 9.0–9.5 during the most titrations of inorganic and organic sodium salts, protonation/deprotonation of the hydroxide layers thus has a limited effect on the surface charging of LDH particles.

3.4. Effect of inorganic salts on the zeta potential

As reported by Lagaly [25] and Sun [23], NaCl salt in a certain range of concentrations does not significantly change the zeta potential of MgAl -LDH particles. The similar phenomenon was also observed in the current research, as shown in Fig. 6A. Except for some variation in the measurement, the zeta potential of both LDHs is almost constant when $[\text{NaCl}]$ is increased from 1×10^{-5} to 3×10^{-3} M. It is acknowledged that the $[\text{NaCl}]$ increase leads

Fig. 6. Plots of the zeta potential of $\text{Mg}_2\text{Al}-\text{CO}_3$ -LDH and $\text{Mg}_2\text{Al}-\text{Cl}$ -LDH particles vs the concentration of (A) NaCl and (B) Na_2CO_3 .

to the ionic strength increase, and slightly reduces the zeta potential (3 mV). Such a decrease in the zeta potential was reported to continue until $[\text{NaCl}] = 0.1$ M [25], however, the zeta potential was still positive even if $[\text{NaCl}] = 1\text{--}3$ M (unpublished work in this group). In sharp contrast, when $[\text{Na}_2\text{CO}_3]$ is added to more than 2×10^{-4} M, the zeta potential of both LDHs starts to decrease rapidly and approaches the point of zero charge (PZC) at ca. 2×10^{-3} M. This phenomenon was also reported by Lagaly et al. and agreed quantitatively (Table 1) [25]. Lagaly et al. also reported the similar relationship between the zeta potential and the concentration of Na_2SO_4 and Na_2HPO_4 [25].

During the titration, the surface anion exchange (Eq. (4)) is expected to affect the zeta potential of LDH particles to a less degree. It is well known that the exchange is mainly dependent on the affinity of LDH for anionic A^- and B^- as well as the relative

Table 1

Concentration (M) of inorganic anions and organic functionalities to reach the point of zero charge (PZC) of two LDHs

	Mg ₂ Al–Cl–LDH	Mg ₂ Al–CO ₃ –LDH
OH [−] , Cl [−]	–	–
CO ₃ ^{2−}	2.2 × 10 ^{−3}	2.0 × 10 ^{−3} (3.0 × 10 ^{−3} in Ref. [25])
C ₁₂ H ₂₅ OSO ₃ [−]	2.1 × 10 ^{−4}	5.1 × 10 ^{−4}
COO [−] in folate	1.2 × 10 ^{−3}	1.1 × 10 ^{−3}
COO [−] in citrate	2.5 × 10 ^{−3}	2.9 × 10 ^{−3}
COO [−] in poly(acrylate)	1.4 × 10 ^{−3}	1.0 × 10 ^{−3}

concentration of A[−] and B[−] in solution. The in situ kinetics investigation reveals that the anion exchange first occurs on the LDH particle edges, then on the basal plane and finally onto the interlayer via diffusion [27], all within a few minutes [27,28]. The sites (A[−] in LDH) available for the exchange on the surface and on the bulk can be estimated from the size and thickness of LDH particles. Approximately, the site concentration in the LDH suspension in this research ([A[−]]) is 8.0 × 10^{−5} M on the surface and 1.5 × 10^{−3} M on the bulk, respectively. Because Cl[−] has a less affinity to LDH than CO₃^{2−}, so the NaCl titration to the Mg₂Al–CO₃–LDH suspension does not cause any noticeable anion exchange. The similar explanation can be also applied to the NaCl titration to the Mg₂Al–Cl–LDH suspension although the [Cl[−]] concentration is higher. The slight decrease of the zeta potential is mainly due to the ionic strength that forces more anions to enter the Stern layer.

In contrast, when Na₂CO₃ solution was injected, the zeta potential of Mg₂Al–Cl–LDH started to decrease and finally became negative at ca. 3 × 10^{−3} M. This is first related to the exchange of nearly all surface and near-edge Cl[−] with CO₃^{2−} at [Na₂CO₃] = 1.0 × 10^{−5} to 1.5 × 10^{−4} M. At above 1.5 × 10^{−4} M, the zeta potential sharply decrease and surprisingly the zeta potential of the Mg₂Al–Cl–LDH particles became negative at [Na₂CO₃] = ca. 3 × 10^{−3} M. Even surprisingly, the zeta potential of Mg₂Al–CO₃–LDH particles became also negative at [Na₂CO₃] = ca. 2 × 10^{−3} M. This seems to contradict to the fact that the zeta potential of salt-free Mg₂Al–CO₃–LDH particles in the suspension is always positive. The zeta potential reversion suggests some other particular process happening with CO₃^{2−} because the pH (ca. 10.5 at [Na₂CO₃] = 2 × 10^{−3} M) and the ionic strength can only slightly reduce the zeta potential (at most by 5–10 mV estimated from the data in Figs. 5 and 6A). We believe that the configuration of some adsorbed CO₃^{2−} on the LDH surface are forcedly changed to allow more CO₃^{2−} to be adsorbed at higher concentrations of CO₃^{2−}. As shown in Fig. 7A, some flatly laid CO₃^{2−} ions (X in Fig. 7A) are forced to be tilt or vertical (Y in Fig. 7A), so that one CO₃^{2−} now does not screen two surface positive charges as usual, but screens only one positive surface charge. Therefore, the surface can hold more CO₃^{2−} and the particle is made negatively charged. Note that the tilt/vertical arrangement of CO₃^{2−} in the interlayer spacing was previously proposed by Ulibarri et al. [29] for $x = 0.44$ in [Ni_{1−x}Al_x(OH)₂](CO₃^{2−})_{x/2}·*n*H₂O. Since CO₃^{2−} anions are very crowded in the interlayer, they are forced to be tilt/vertical in the interlayer. Such a configurational rearrangement of CO₃^{2−} in the interlayer may also occur on the surface when the CO₃^{2−} concentration is high enough. If this postulation is true, then only ca. 4% of surface CO₃^{2−} doing so can make the surface negatively charged based on the simulation result that the net positive charge density is 0.01 C/m² while the inherent surface charge density is 0.24 C/m² [22]. In addition, this model can also explain the reverse effect of Na₂SO₄ and Na₂HPO₄ on the zeta potential at a similar concentration observed by Lagaly et al. [25]. In these two cases, the tetrahedral anions (SO₄^{2−} or HPO₄^{2−}) can naturally stand on the surface to allow more anions to enter the Stern layer, and result in the PZC of LDH particles at an even lower anion concentration [25].

Fig. 7. Adsorption models of (A) carbonate and (B) dodecyl sulfate on the LDH surface.

3.5. Effect of organic salts on the zeta potential

Figs. 8A–8D demonstrate the zeta potential change of LDH particles with the concentration of various organic anions. To compare the effect of these organic anions on the similar base, the concentration is expressed as the anionic group concentration. In general, the zeta potential of LDH particles is slightly changed at the lower concentrations (1 × 10^{−5} to ca. 1–8 × 10^{−4} M), then has a steep decrease to the negative value in a narrow concentration range. For example, when dodecyl sulfate concentration was increased from 1.0 × 10^{−5} to 3.8 × 10^{−4} M, the zeta potential of Mg₂Al–CO₃–LDH particles was decreased from 24.5 to 16.2 mV. However, as the concentration was further increased from 3.8 × 10^{−4} to 6.3 × 10^{−4} M, the zeta potential was reversed from 16.2 to −14.5 mV (Fig. 8A). The phenomenon is very much similar for all other cases (Figs. 8B–8D) except for the titration with dodecyl sulfate to the Mg₂Al–Cl–LDH suspension. At around 1.0 × 10^{−4} M of dodecyl sulfate, the zeta potential started to sharply decrease and then changed to a negative value as the concentration increased to 2.0 × 10^{−4} M.

As summarized in Table 1, the concentration of organic functionalities that leads to the point of zero charge (PZC) is similar (1.0–2.9 × 10^{−3} M) except for dodecyl sulfate. The PZC concentration of dodecyl sulfate (2.1–5.1 × 10^{−4} M) is significantly lower, which can be ascribed to the higher affinity of its sulfate group (−OSO₃[−]) than carboxylate (COO[−]) and in particular to the stronger hydrophobic interactions between the long hydrocarbon chains (dodecyl, −C₁₂H₂₅). As schematically outlined in Fig. 7B, sulfate group can readily replace the surface Cl[−] in Mg₂Al–Cl–LDH particles, starting on the edge and then on the basal plane [27]. When the concentration of dodecyl sulfate is increased to 1 × 10^{−4} M, most surface Cl[−] (8.0 × 10^{−5} M) are exchanged. Under this assumption, the hydrocarbons chains are aligned to face the water, forming a tentative high-tension surface (tailing region of U in Fig. 7B). To release the surface tension, the further injected dodecyl sulfate will interact with these hydrocarbon chains via hydrophobic

Fig. 8. Plots of the zeta potential of Mg₂Al-CO₃-LDH and Mg₂Al-CI-LDH particles vs the concentration of (A) dodecyl sulfate, (B) folate, (C) citrate and (D) polyacrylate.

forces to form the micelle-like structure, such as the inter-digitated bilayer (region V in Fig. 7B). The formation of such a bilayer structure (micellization), or say, the organic species self-assembly on the particle surface, results in the negatively charged surface when ca. 4% more dodecyl sulfates are micellized on the surface.

In the case of Mg₂Al-CO₃-LDH, as CO₃²⁻ has a higher affinity for LDH than Cl⁻, its exchange with dodecyl sulfates can only significantly take place at a higher concentration ($3\text{--}4 \times 10^{-4}$ M), and as a result, its PZC concentration (5.1×10^{-4} M) is much higher than that in the case of Mg₂Al-CI-LDH (2.1×10^{-4} M). Note that the hydrophobic interactions between the long hydrocarbon chains have great contribution to the affinity of the organic anions to LDH [30], as reported for dodecylbenzene sulfonate that has an affinity comparable with CO₃²⁻ [31]. The hydrophobic interactions inter-connect many dodecyl chains into a bunch (V in Fig. 7B) so that each organic anion shows a stronger affinity to LDH [30,31].

For the other three organic anions, the PZC concentration is much higher, which can be ascribed to two factors: (i) -COO⁻

group has a less affinity than -OSO₃⁻ [32], so that the adsorption/exchange occurs at a higher concentration. This is evidenced by the fact that the zeta potential only significantly decreases at above $0.8\text{--}1.0 \times 10^{-3}$ M of anionic groups; and (ii) the hydrophobic interactions among the short hydrocarbon chains or small hydrocarbon regions are much weaker than those among the straight dodecyl chains (-C₁₂H₂₅), so that the micellization occurs at a high concentration. However, each of these anions has two or more anionic groups in one moiety, which helps to readily negatively charge the LDH particles because one or more anionic groups can directly face to the aqueous phase from the LDH particle surface. Therefore, even the affinity of -COO⁻ group to LDH is weaker than Cl⁻ and CO₃²⁻,¹ a small extra portion of exchange/adsorption (>4%) is enough to make the LDH particles negatively charged.

¹ Note: In the exchange of LDH-Cl with CH₃COO⁻, we found that the exchange degree is very small in one exchange experiment. If we continue to exchange for 3–4 times (exchange–separation, then exchange–separation, etc.), significant amount

It is worth mentioning that when the zeta potential is down to close to zero, the LDH particles severely agglomerate. In general, the LDH particles start to aggregate at a salt concentration just around the PZC concentration [25] that is also called as the critical coagulation concentration.

4. Conclusions

In conclusion, the dynamic effect of pH, inorganic and organic salts on the surface charging of $\text{Mg}_2\text{Al}-\text{Cl}$ -LDH and $\text{Mg}_2\text{Al}-\text{CO}_3$ -LDH particles has been investigated. The decrease of pH from 11.0 to 5.5 has little effect on the zeta potential of $\text{Mg}_2\text{Al}-\text{Cl}$ -LDH but significantly increases that of $\text{Mg}_2\text{Al}-\text{CO}_3$ -LDH particles due to the conversion of CO_3^{2-} to HCO_3^- at pH 6–10. The addition of NaCl does not obviously change the zeta potential of both LDHs, but Na_2CO_3 reduces the zeta potential and even to the negative value, probably relevant to the re-orientation of some adsorbed carbonate on the surface. All the organic anions investigated can negatively charge LDH particles, which can be attributed to the micellization or self-assembly of adsorbed/exchanged organic anions on the LDH surface although these organic anions have the different composition and structure.

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