



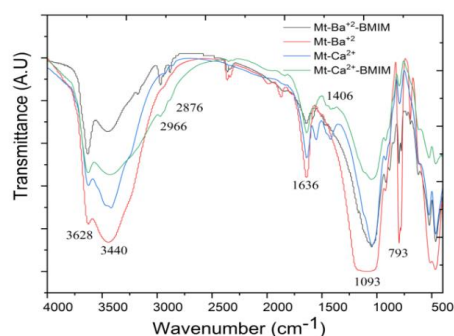
EFFECT OF INTERLAYER CATIONS ON THE ADSORPTION OF IONIC LIQUID ON MONTMORILLONITE CLAYS: COMPARATIVE STUDY

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Industries are the most important resource of water pollution due as a result of toxic pollutants including surfactant or ionic liquids. It becomes urgent to propose low cost and environmentally friendly involving the use of local resources. Here, one of the main ionic liquids (BMImCl) were intercalated into three alkaline-earth, Mg^{2+} , Ca^{2+} , and Ba^{2+} exchanged montmorillonites. For all samples interlayer spacing after intercalation are similar about 13 Å as measured by X-ray diffraction. These findings are compared with previous results on similar montmorillonite exchanged with every type of alkali cations, i.e. Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ . The basal spacing of intercalated montmorillonite increased as the ionic potential (Z/R) is increased. The FTIR is another tool to confirm the differences between modified and unmodified montmorillonite samples. More specifically, the results showed that the formation of new bands of vibrations ($1400\text{--}1500\text{ cm}^{-1}$) and ($2850\text{--}2900\text{ cm}^{-1}$). Thermal measurements indicate that homoionic clay display two distinct regions. (I) from room temperature to $160\text{ }^{\circ}\text{C}$ corresponding to physical adsorption and removal of water of hydration, (II) dehydroxylation of the silicate structure in the temperature range of $160\text{--}700\text{ }^{\circ}\text{C}$.



INTRODUCTION

Montmorillonite (Mt) is one of the main smectite groups, formed of tetrahedral sheets sandwiched between two parallel octahedral sheets of very fine particle size ($< 2\text{ }\mu\text{m}$). Montmorillonites have unique physical and chemical characteristics that make them effective at absorbing both organic and inorganic pollutants, such as a high cation exchange capacity (CEC) and an important specific surface area. Numerous industrial applications have made major use of

montmorillonites, they serve as raw materials in therapeutic and pharmaceutical products. Modified montmorillonite have been used for treating topical conditions utilizing its antimicrobial activity.¹

Ionic liquids (ILs) are organic salts with a melting point under $100\text{ }^{\circ}\text{C}$, and high thermally stability.² Low vapour pressures,³ they present a desirable alternatives for conventional solvents for many organic, inorganic compounds and are therefore frequently utilized as green solvents for a variety of applications.^{2,4,5} Ionic liquids are created when organic cations that contain nitrogen,

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phosphorus, or sulphur, such as alkyimidazolium, alkyipyridinium, alkylphosphonium, or alkylammonium, combine with organic or inorganic anions. (BF_4^- , PF_6^- , Cl^- , Br^- , etc.).⁶ It is really known that many ionic liquids are soluble in water. Therefore, the release of ionic liquids containing wastewater should be strictly controlled to reduce the bad effect on biological systems. Numerous studies have shown that ionic liquids' toxicity and ecotoxicity may have an effect on the environment.⁷ It is thus needed to find solutions for their removal. Such as organic wastes ionic liquids, can be treated by different mechanisms including activated carbons,⁸ layered zirconium phosphates⁹ and nano-silica,¹⁰ Adsorption is typically regarded as an affordable and efficient alternative approach for eliminating pollutants such ionic liquids especially combined with appropriate regeneration steps. Recent studies revealed the intercalation of many ionic liquids into the interlamellar spaces of clays. Kaolinite was used for the adsorption of an ethyl-pyridinium chloride¹¹ and pyrrolidinium halides.¹² Montmorillonites were used for the intercalation of many ionic liquids, as example imidazolium,¹³⁻¹⁵ pyridinium¹⁶ or phosphonium salts.¹⁷ The goal of this present work was to investigate the adsorption capacity of reference montmorillonite, exchanged with the most common alkaline-earth cations, that is Mg^{2+} , Ca^{2+} , and Ba^{2+} towards one of the main pollutants ionic liquids, 1-Butyl-3-methylimidazolium Chloride (BMIMCl) through a cation exchange mechanism. We first present the data on three homoionic, Mg^{2+} , Ca^{2+} , and Ba^{2+} , alkaline-earth exchanged montmorillonites, and then we compare these findings to those on montmorillonite exchanged with the entire series of alkali metal cations, using the exact same experimental methodologies and materials.¹⁸

EXPERIMENTAL

1. Materials and methods

The clay used in this work was taken from Crook County (Wyoming) and purchased from the Source Clays Repository (Clay mineral Society ref: Srce Clay SWy-2, for more information see <http://www.clays.org/>). This clay mineral has the chemical formula ($\text{Si}_{17.89} \text{Al}_{3.34} \text{Fe}_{0.42} \text{Mg}_{0.56} \text{Ca}_{0.52} \text{Na}_{0.14} \text{K}_{0.01}$).¹⁹ According to reports, it has a cation exchange capacity (CEC) of about 75 meq per 100 g.²⁰ The clay fraction ($\leq 2 \mu\text{m}$) that was obtained by dispersion, sedimentation, and centrifugation with a was used in the current study.

Exchanged montmorillonites with Mg^{2+} , Ca^{2+} , Ba^{2+} cation were obtained by dispersing 1 M of XCl_2 solution (where $X = \text{Mg}, \text{Ca}, \text{Ba}$) for 24 h, followed by centrifugation. This operation was repeated three times, and finally, the powder was washed with water until no trace of chloride ions was detected by AgNO_3 test.^{21, 22} Finally, centrifugation and air drying are used to separate the powder from the liquid phase. The so obtained samples are here after referred to as Mt-X. The 1-Butyl-3-methylimidazolium chloride (BMIMCl) (CAS#:79917-90-1), was purchased from Tokyo chemical industry Co, Ltd. (Japan).

2. Ionic liquid adsorption into Mt

50 mg of homoionic Mt was dispersed in 10 mL (or 30 mL) of water with BMIMCl concentrations from 2.5 to 5.5 $\text{mmol}\cdot\text{L}^{-1}$ for the isotherm study or 1 $\text{mmol}\cdot\text{L}^{-1}$ for the kinetic study. The mixture was stirred for 20 min at room temperature. For kinetic study, the contact time was from 3 to 30 min. The supernatant was removed to measure the BMIM^+ concentrations by absorbance at the wavelength of 211 nm, using spectrophotometer (UviLine9400-SECOMAM).

3. Characterization

XRD patterns of the prepared Mt were recorded using a Philips X-Pert diffractometer with $\text{Cu-K}\alpha$ radiation and 2θ incident rays. Data were recorded by step scanning 0.02° per 55 s from 3° to 80° . The interlayer distance was calculated, for each sample, from the position of the d_{001} ray. In order to evaluate the thermal stability of the homoionic clay, thermogravimetric analysis (TGA) and differential thermal analyses (DTA) were performed with a (LABSYS evo) instrument using 40 mg samples. In a nitrogen atmosphere, the samples were heated at a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature to 1000°C . Fourier Transform-infrared (FTIR) measurements were acquired on a BIO-RAD FTS-40 Spectrometer. FTIR spectra were collected with resolution of 1 cm^{-1} in a wave number range of $4000\text{--}400 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

1. X-ray Diffraction Analysis

XRD analyses were performed on the three alkaline-earth exchanged montmorillonites are shown in Fig.1. Examination of the diffractograms indicates that the remaining impurities consist of quartz (Q). The interlayer distance, that is d_{001} given in Table 1, demonstrates that our samples are hydrated under room conditions and is in the same range of that stated in the literature. These values of d_{001} correspond to the adsorption of two (respectively one) layers of water molecules in the interlayer space of the Mg^{2+} and Ca^{2+} (respectively Ba^{2+}) exchanged montmorillonites.²³⁻²⁵

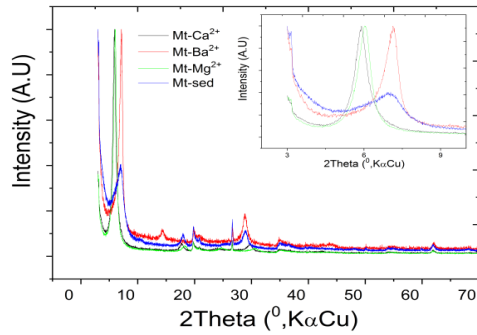


Fig. 1 – X-ray diffraction patterns of montmorillonite exchanged with alkaline-earth metals under room conditions.

Table 1

d_{001} determined from XRD Pattern Obtained on the homoionic alkaline-earth exchanged montmorillonites under room conditions

Sample	d_{001} (Å) (our study)	d_{001} (Å) (others)
Mt- Mg ²⁺	14.56	15.1 ; 15.0 ^{23,25}
Mt- Ca ²⁺	14.96	15 ; 15.05 ^{23,25}
Mt- Ba ²⁺	13.31	12.4 ; 12.72 ^{23,25}

After adsorption of BMIM⁺, the characteristic peak was shifted to higher 2θ values (Fig. 2). Leading a decrease of the interlayer spacing (Table 2) .

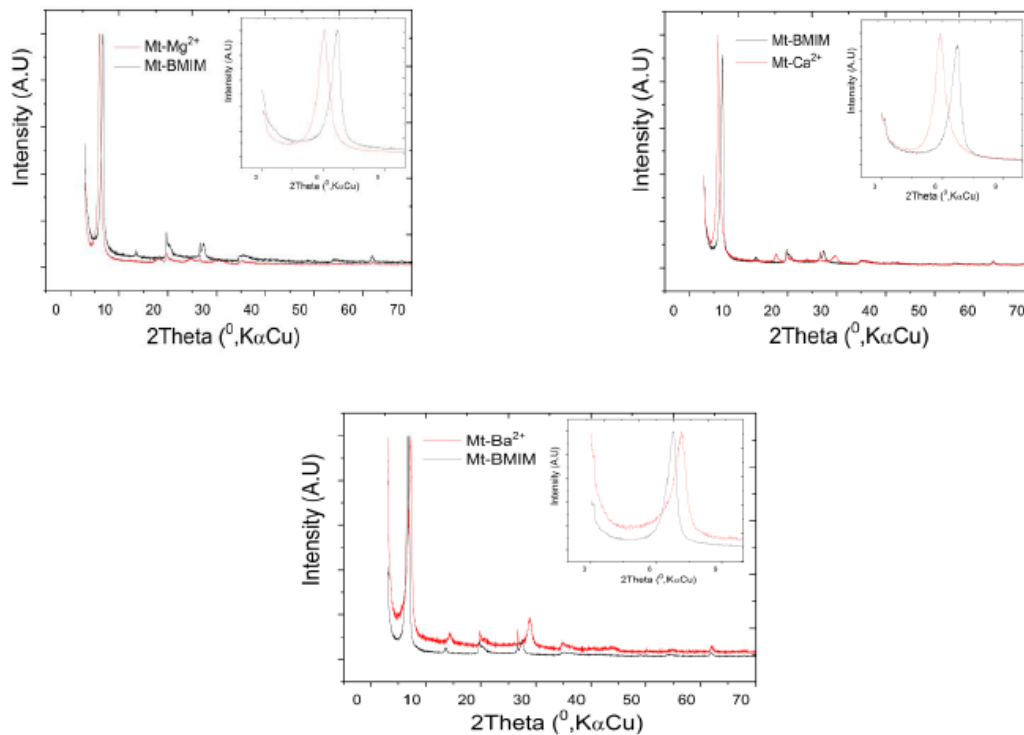


Fig. 2 – X-ray diffraction patterns of montmorillonite samples: before and after adsorption of BMIM.

Table 2

d-Spacings of the homoionic Mt and Mt-BMIM obtained from XRD patterns

Sample	Mt-Mg ²⁺	Mt-Ca ²⁺	Mt-Ba ²⁺
Mt (Å)	14.56	14.96	13.31
Mt-BMIM (Å)	13.17	13.06	13.03

The values of interlayer spacing are similar about 13 Å for all samples. Are in the same range than the one previously reported but with another type of montmorillonite.¹³ This confirms that the initial interlayer cations were replaced by BMIM⁺ (Fig. 3). These results suggest to the high affinity between divalent cation and water molecules which decreases their interaction with the Mt. Thus, the exchange with the BMIM⁺ is favoured.

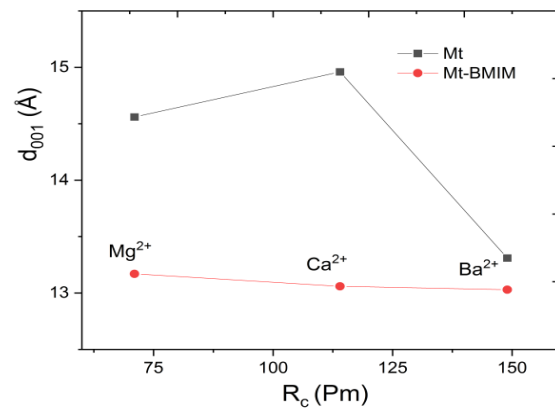


Fig. 3 – Evolution of basal spacing for alkali metals montmorillonites as a function of cation radius before and after exchange of BMIM⁺.

2. FTIR analysis

The infrared spectra of homoionic montmorillonite exhibited similar bands in the region 4000–400 cm^{-1} (Fig. 4). The large band observed at 1093 cm^{-1} on all the spectra, were attributed to the Si–O stretching vibration of montmorillonite.²⁶ The vibration bands of water gave two signals (Fig. 4) Broad band at 3440 cm^{-1} attributed to the OH asymmetric and symmetrical stretching vibrations, and a peak at 1636 cm^{-1} assigned to the bending vibrations.²⁷ The peak at 3628 cm^{-1} was attributed to the hydroxyl groups of the montmorillonite layer.²⁸

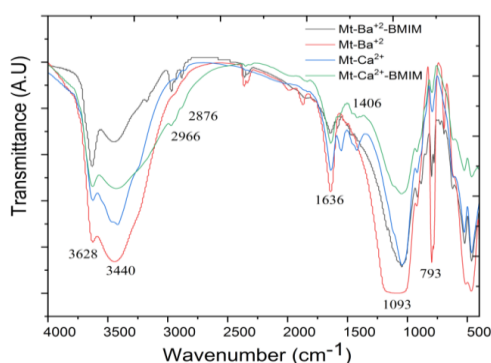


Fig. 4 – FTIR spectra in the range 4000–400 cm^{-1} of Mt samples: before and after adsorption of BMIM.

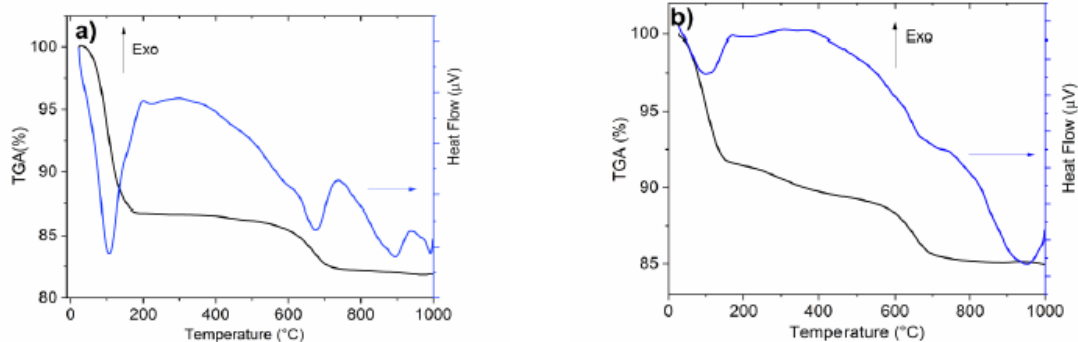


Fig. 5 – TGA and DTA curves of the: a) Mt-Ca²⁺ and b) Mt-Ba²⁺.

Table 3

Mass loss during dehydration and dehydroxylation of the Mt-Ca²⁺ and Mt-Ba²⁺ samples

Sample	Dehydration	Dehydroxylation
	25–160 °C	160–675 °C
Mt-Ca ²⁺	12.85 %	16.32 %
Mt-Ba ²⁺	08.3 %	14.10 %

The mass loss observed at temperatures ranging between 160–675 °C corresponds to the water release originating from OH groups structurally bound in the lattice. TG results

Infrared spectra of intercalated montmorillonites (Fig. 4). Indicated the presence of the characteristic bands of the ionic liquid. The small peaks in the region 1400–1500 cm^{-1} were characteristic of the asymmetric bending vibrations of the CH₂ and CH₃ groups of the alkyl chains,¹⁸ the asymmetric and symmetric signals, characteristic of the hydrocarbon chain are observed with a varying intensity in the 2850 – 2900 cm^{-1} region.¹⁸ However, for these two materials, the band observed at 1636 cm^{-1} was broadened suggesting the presence of a small amount of water.

3. Thermo gravimetric analysis (TGA, DTA)

Thermogravimetric (TGA) analysis have been used to probe the thermal stability of Ca²⁺ and Ba²⁺ exchanged montmorillonite, and the result was shown in (Fig. 5, Table 3) presents an overview of the mass changes corresponding to samples dehydration and dehydroxylation. In the temperature range of about 25–160 °C a water took place. Mass loss of Mt-Ca²⁺ in 25–160 °C was 12.85 %, 8.2 % more than that of Mt-Ba²⁺ (Fig. 2), illustrating that Ca²⁺ in Mt-Ca²⁺ was more hydrated than Ba²⁺ in Mt-Ba²⁺.

presented in this study agree well with findings of other authors,²⁹ where they suggested that the amount of interlayer water depends on hydration energy of the adsorbed cations and on hydration of the surface, and that TG curves can be interpreted to give relative values for these amounts of water. The result indicated less amount of inter-layer space water in Mt-Ba²⁺ in comparison to Mt-Ca²⁺, suggesting weaker interaction force between Ba²⁺ cation and water molecule than that between Ca²⁺ and water molecules; that is, Ba²⁺ was less hydrated than Ca²⁺.

The differential thermal analysis (DTA) curves showed a similar trend within 25–160°C (Fig. 5). The endothermic reaction, which may be due to water that is adsorbed onto the external surface and/or coordinated to exchangeable interlayer cations and adsorbed between the clay mineral layers³⁰. It is also in agreement with XRD data (Fig. 1). In the second stage, the occurrence of another peak at about 675 °C was due to the dehydroxylation of the clay lattice -OH groups.

4. Adsorption of BMIMCl on Mt

The kinetic study aims to investigate the influence exchangeable cation on the adsorption of BMIMCl and determine the time required to reach equilibrium for further experiments. The adsorption kinetics of BMIMCl onto Mt- Mg²⁺, Mt- Ca²⁺ and Mt- Ba²⁺ are reported on (Fig. 6).

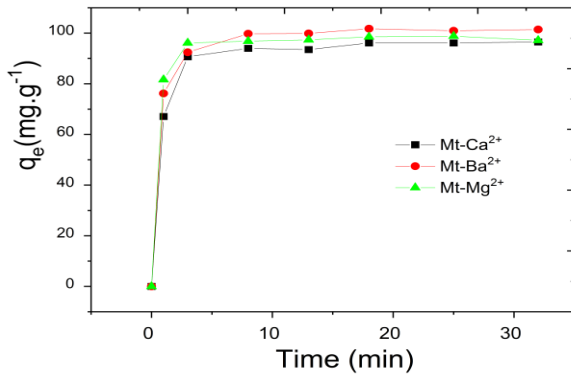


Fig. 6 – Kinetics of BMIM intercalation on Mt samples ($m_{\text{adsorbent}} = 0.05 \text{ g}$, $[\text{BMIM}] = 1 \text{ mmol}\cdot\text{L}^{-1}$).

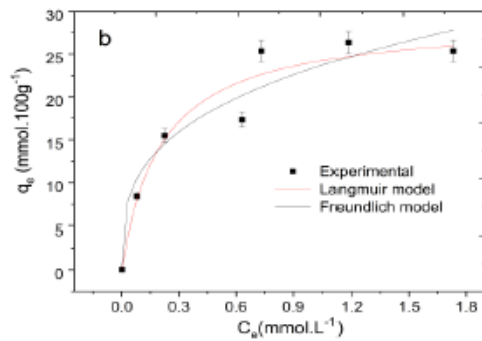
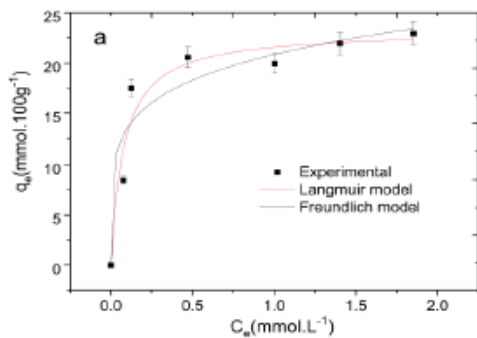


Fig. 7 – Adsorption isotherms of BMIM onto homoionic Mt: a) Mt-Mg²⁺ and b) Mt-Ca²⁺.

Table 4

Fitting parameters obtained for Langmuir and Freundlich isotherms

Sample	Langmuir model			Freundlich model		
	q_m (mmol·100g ⁻¹)	K_L (L·mmol ⁻¹)	R^2	K_F	n	R^2
Mt-Mg ²⁺	23.28	12.74	0.95	20.86	5.3	0.91
Mt-Ca ²⁺	29.12	4.75	0.95	23.35	3.15	0.93

The equilibrium is reached after 20 min whatever the interlayer cation. To go further, the influence of interlayer cation on BMIMCl isotherm of adsorption was investigated. The adsorption isotherms exhibited similar profiles for all interlayer cations. The experimental data were fitted to with two commonly used models (Fig. 7). The Langmuir model³¹ equation (1) assumes the formation of a monolayer onto homogeneous surface with a finite number of sites. It also assumes that at the equilibrium both adsorption and desorption occurs.

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (1)$$

where C_e (mg·L⁻¹) is the equilibrium concentration of IL in solution, q_e (mg·g⁻¹) the adsorption capacity at equilibrium, q_m (mg·g⁻¹), the maximum adsorption capacity and K_L is the effective dissociation constant.

The Freundlich isotherm is an empirical model equation (2) usually used for heterogeneous adsorption.³² The limitation of this model is that the amount of adsorbed molecule increases indefinitely with the concentration of in the solution.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where q_e (mg·g⁻¹) is the adsorption capacity at equilibrium, C_e (mmol·L⁻¹) is the equilibrium concentration in solution, and K_F and n are the physical constants. The calculated parameters of Langmuir, Freundlich isotherms for the adsorption of BMIMCl onto Mt-Mg²⁺ and Mt-Ca²⁺ are listed in Table 4.

However, from these data the adsorption of BMIMCl onto Mt samples was fitted well to all of the isotherm models as indicated by the correlation coefficient (R^2) values. For the Butylmethylimidazolium the adsorption capacities are not enhanced by the presence of divalent interlayer cation. Indeed the BMIM⁺ adsorbed Mt-Mg²⁺ and Mt-Ca²⁺ were 23.272 mmol·100g⁻¹ and 29.122 mmol·100g⁻¹, respectively. These values of adsorption capacity are lower than the one reported for BMIM⁺ (70 mmol·100g⁻¹) on montmorillonite exchanged with the whole series of alkali cations.¹⁸

5. Comparison between alkaline-earth and alkali exchanged montmorillonites

Comparison of data obtained in this study with that previously published on the alkali-exchanged montmorillonites.¹⁸ Verify that the exchange process, as depicted in Fig. 8, is influenced by the interlayer cation's nature.

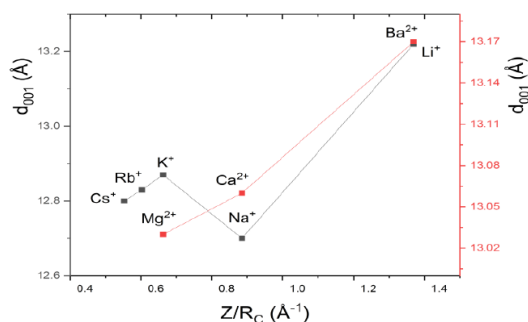


Fig. 8 – Evolution basal spacing as a function of Z/R_C with Z and R_C the cation valence and radius, respectively.

For the so-called kosmotrope cations, that is Mg²⁺, Ca²⁺, Li⁺, Ba²⁺, and Na⁺, interlayer distance d_{001} , vary similarly, that is they increase with the cation potential energy. Theng *et al.* described the ionic potential (Z/R) as a measure of the influence a cation can exert over neighboring molecules.³³ More particularly, we can notice that the d_{001} , values of the Mt-Ba²⁺ and Mt-Li⁺ samples are comparable, the parameter Z/R_C thus appears an important characteristic correlated to the adsorption in montmorillonite exchanged with kosmotropes cations. These findings agree well with previously reported with adsorbed water molecules in same montmorillonite.²¹

CONCLUSIONS

This work demonstrates that homoionic montmorillonite is a potential adsorbent for ionic

liquid, the intercalation processes was demonstrated by XRD analysis, whatever the interlayer cation basal spacing after intercalation are similar about 13 Å. The presence of butylmethylimidazolium in the clay surface was independently confirmed by FTIR, which manifested as the appearance new bands of vibrations. Comparison between mono- and divalent interlayer cation, shed some light on the relative effect of both the charge and the size of interlayer cation of montmorillonite (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺, and Ba²⁺).

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