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Zeta Potentials of Sepiolite Suspensions in Concentrated Monovalent Electrolytes

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Abstract: Sepiolite is a hydrated magnesium silicate with a fibrous structure. It undergoes acid-base interactions around the natural pH of 8.5. The zeta potential (zp) of sepiolite depends on the type, the chemical, and the mineralogical composition of sepiolite and more importantly the ionic environment of the suspensions. In this study, electrokinetic properties of sepiolite have been determined. A series of systematic zeta potential measurements have been performed to determine the isoelectric point (iep), the potential determining ions (pdi), and the effect of monovalent ions on the zeta potential of sepiolite. The electrokinetic behavior of sepiolite was examined in the presence of monovalent ions to identify if they adsorb through ion exchange or get incorporated in the diffused layer. A schematic ion adsorption/ion exchange model which illustrates the arrangement of monovalent ions in the electrical double layer of sepiolite is proposed.

Keywords: Sepiolite, electrokinetics, zeta potential, electrolytes, adsorption, ion exchange

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INTRODUCTION

The electrokinetic properties of fine particles in an aqueous solution such as the isoelectric point (iep) and potential determining ions (pdi), play a significant role in understanding the adsorption mechanisms of inorganic and organic species at the solid/solution interface. They also govern flotation, coagulation, and the dispersion properties in suspended systems. In flotation, these properties are used to understand the mode of collector adsorption on minerals, selection of appropriate flotation reagents, and the examination of activation mechanisms (1, 2). Effective coagulation, an important step in many solid-liquid separation processes such as wastewater treatment systems, requires an understanding of the particle zeta potential (zp) and isoelectric point of the system (3, 4). In the ceramics industry and in the design of nanocomposite materials, especially in clay-water colloidal systems, the electrokinetic properties of the colloidal particles are critical in defining the optimal conditions of a well-dispersed system.

Sepiolite has an ideal formula of (Si_{12}) $(Mg_9)O_{30}(OH_6)$ $(OH_2)_4$ $6H_2O$ according to the Nagy-Bradley model (5). Palygorskite and attapulgite are synonymous terms for the same hydrated magnesium aluminum silicate mineral. Sepiolite is almost structurally and chemically identical to palygorskite except it has a slightly larger unit cell (6). However, aluminum in sepiolite has been considerably substituted by magnesium in the octahedral layer such that it gives moderately high layer charge. Structurally, it is formed by the alternation of blocks and tunnels that grow up in the fiber direction. Each structural block is composed of two tetrahedral silica sheets sandwiching a central sheet of magnesium oxide-hydroxide (7). This unique fibrous structure with interior channels (3.6×10.6 Å) allows the incorporation of organic and inorganic ions into the structure of sepiolite. Serna and Van Scoyoc (8) calculated the total surface area of 900 m^2/g of which 500 m^2/g is the external surface area and 400 m^2/g the internal surface area based on the channels of 3.6×10.6 Å in size.

Zeta (ζ) potential (zp) is an intrinsic property of mineral particles suspended in a liquid. It determines the strength of the electrical double layer (EDL) repulsive forces between particles and controls the stability of a colloidal system. The zp is known as the measurable surface potential of a particle at the shear plane. Clay minerals exhibit highly interesting electrokinetics features. While the montmorillonite particles bear a negative charge generated by substitution of lattice ions that is largely independent of the aqueous composition, the edge surfaces show a pH-dependent charge. The zp of montmorillonite particles is negative throughout the pH region and basically independent of the pH due to the dominant role of constant negative charge of faces (9–11); this inference is logical considering that only about 1% of the total surface area is attributed to edges (9, 12). The cation exchange capacity observed for sepiolite is attributed to the isomorphic substitution of Si^{4+} by trivalent Al^{3+}, and broken bonds at the fiber edges. These broken bonds particularly in well-crystallized sepiolites, are considered an important source of ion exchange capacity (13). Discussions of the electrokinetic behavior of sepiolite, to our knowledge, are limited in the literature (14).

In this study, sepiolite samples of different chemical compositions are subjected to zp measurements with the objective of understanding the charging mechanism of sepiolite in the absence and presence of monovalent electrolytes.

MATERIALS AND METHODS

Materials

The sepiolite samples used in this study were received from the Sivrihisar region of Turkey. Two other commercial samples of Tolsa (Pangel S15 and Pangel S9) were also used as references. The K series referred to in Table 1 as K1, K2, K3, and K4 are brown in color. X-ray diffraction in conjunction with the chemical analysis using ICP for the Sivrihisar samples generally indicated that calcite and dolomite are the major impurities. The SiO_2/MgO values calculated from Table 1 for the Sivirihisar samples vary in the range of 2.10–2.37 which encompasses the theoretical value of $55.6:24.99 = 2.23$, whereas the Tolsa samples yield a range of 2.48–2.52. The practical values reported in the literature for the SiO_2 and MgO are in the range of $53.9 \pm 1.9\%$ and 21–25%, respectively (15).

All chemicals used for pH adjustment (NaOH and HCl) and monovalent salts, i.e. NaCl, KCl, LiCl, NH_4Cl, and CsCl were of analytical grade. Distilled and deionized water with a conductivity value of less than 2×10^{-6} mhos/cm was used in all experiments. Experiments were conducted at 25°C.

Table 1. Chemical analysis of various sepiolites

Item	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	CaO %	Na_2O %	K_2O %	TiO_2 %	LOI %	CEC Meq/100 g
Sample										
K1	51.29	1.37	0.58	22.57	0.26	0.09	0.21	0.08	23.6	17.4
K2	45.75	1.37	0.591	21.89	3.31	0.09	0.22	0.08	26.2	16.4
K3	50.61	1.99	0.81	21.34	0.28	0.16	0.36	0.11	24.6	25.6
K4	51.83	1.52	0.70	24.20	0.12	0.12	0.33	0.08	21.0	18.4
Beige	48.82	1.17	0.51	22.28	1.17	0.01	0.19	0.07	25.7	24.6
Pangel S15	53.93	2.29	0.76	21.39	0.28	0.09	0.41	0.11	20.6	—
Pangel S9	54.07	2.42	0.90	21.79	0.30	0.12	0.43	0.11	19.6	20.5

Methods

Sepiolite ranging from 0.1 to 10 g was suspended in 100 ml of distilled water of known pH and mixed with a magnetic stirrer. The pH of suspensions was periodically checked to follow the changes in pH as a function of time. Hydrochloric acid was slowly added until the target pH value was attained. The zp was measured as fast as possible followed by a second pH measurement. The difference between the measured and set value was divided by two and added to the set pH value.

Electrokinetic measurements were carried out using a Zeta Meter 3.0 (Zeta-Meter, Inc., 765 Middlebrook Avenue, Staunton, VA USA, www.zeta-meter.com) equipped with the microprocessor unit. It automatically calculates the electrophoretic mobility of particles and converts it to the zeta potential by a built-in microprocessor unit which uses the Smoluchowski equation. The maximum ionic strength used in all measurements was below 0.1 M/l, which corresponds to a double layer thickness ($1/\kappa$) of about 10 Å. Since the particle sizes used for the measurement of zeta potentials are a few micrometers in size and solubility of associated cations in sepiolite is over 10^{-3} M/l, the condition of $\kappa\alpha \geq 1$ is obeyed under all conditions and the Smoluchowski equation is valid. In addition, the range of zeta potentials from pH 2 to 9 remains below 25 mV; this effect minimizes retardation and relaxation effects and the overall error remains within an acceptable range (3).

One major problem with measuring zeta potential in relatively concentrated solutions is that the solution becomes turbid due to the fineness and color of the sample. If the material is coarse and the color is white, the visibility can be tolerated to a greater extent. In our case, the turbidity level above 0.2 g in 100 ml of solution was found to disturb the visibility. Therefore, the validity of zp measurements at high solids concentrations and under adsorption test conditions were tested in two ways, i.e. direct and centrifuge techniques, to avoid these two problems and also to get reliable zp values.

In the direct technique a predetermined amount (0.2 to 5 g solids) of sepiolite was conditioned in 100 ml of distilled water for 10 minutes. The suspension was kept still for 5 minutes to let particles larger than about 30 microns, if present in solution, settle. Since the material was ground to minus 30 microns, practically very few particles settled in the suspension. It is interesting to note that at solids concentrations higher than about 0.2% the resultant turbid solution hampered the visibility of sepiolite particles in the zeta potential cell. Therefore, for higher solids concentrations or to conduct tests under the conditions of adsorption (3% solids), a centrifugation technique discussed below was developed.

To resolve the visibility problem, actual suspensions after the adsorption tests were centrifuged. After solid/liquid separation, the clear supernatant of about 25 ml in volume was transferred to the electrophoresis cell while a sample of several mg in weight from different parts of the well-mixed sepiolite bed (settled deposit) was taken and mixed with the supernatant. This procedure enabled us to satisfy the percent solids requirement, helped utilize the entire sample, as well as provided an excellent visibility. The validity of this procedure was tested at 0.1% solids suspensions where both direct and centrifuge techniques could be used. The zp results reported in this study were consequently conducted using the centrifuge technique.

Each data point is the average of approximately 10 measurements. If the standard deviation is more than 3%, the measurement was repeated. Zeta potential measurements were carried out as a function of percent solids concentrations and pH.

The magnitude of the adsorption/ion exchange in the presence of monovalent salts and its prevailing mechanisms were studied with chloride salts of alkali metal ions: Li^+, Na^+, K^+, Cs^+ and NH_4^+. The adsorption tests were conducted in 40 ml glass vials with Teflon-lined caps using 1.2 g sepiolite and 40 ml electrolyte solution and conditioned for one hour on a vibrating shaker at 400 rpm. The suspensions were centrifuged and the supernatants were analyzed for alkali metal ion concentration using ion selective electrodes (Orion brand Na, K, Li, and NH_4 electrodes). Mg was analyzed by Atomic Absorption Spectrometer (Philips PU 9100 X).

All samples for adsorption measurements have been reduced to below 30 μm. The d_{50} value (the particle size at which 50% of the material passes through this particular sieve size), which together with the top size characterizes the particle size distribution, varies in the range of 1.8 to 4.9 μm for all samples. A Fritch Size Analyzer was used for particle size analysis. Fritsch Analysette 22 Compact model particle size analyzer is a laser-light scattering instrument which utilizes the physical principle of the scattering of magnetic waves for the determination of particle size distribution. A parallel-light is scattered to fixed spatial angles, which depend on the particle size and the optical properties of the particle.

RESULTS AND DISCUSSION

pH Profiles of Sepiolite Suspensions

Figure 1 shows the pH profile of sepiolite suspensions for different initial pH values as a function of time. It is seen that sepiolite attains an equilibrium pH value of 8.5 in 2 min. at equilibrium pH conditions. When the initial pH value of suspension is adjusted to 3.0, the equilibrium pH value of 8.5 is attained after approximately 10 min. Similar but slower equilibrium conditions were reported for clinoptilolite (16). Under similar conditions, montmorillonite is known to attain its equilibrium pH in about 2 hours (17). This indicates that sepiolite is alkaline in character and undergoes acid-base reactions in the vicinity of pH 8.5.

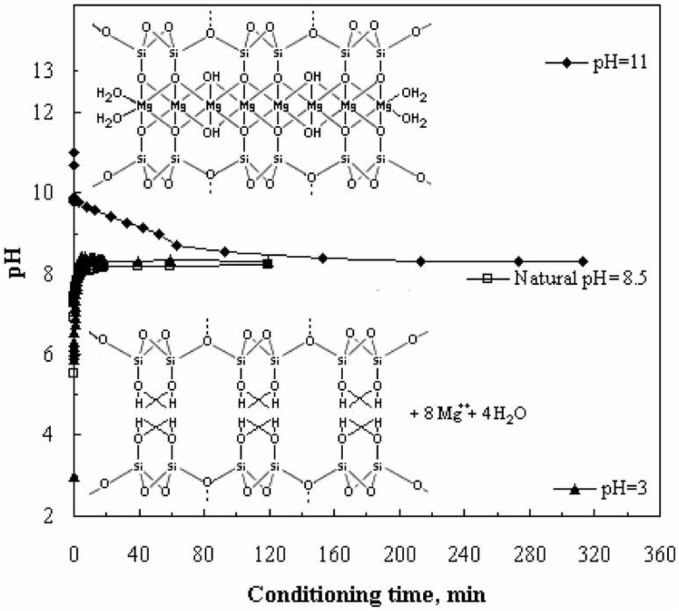

Figure 1. Effect of conditioning time on equilibrium pH of K4 sepiolite suspensions.

The rise of pH from 3 to 8.5 is attributed to the rapid dissolution of Mg^{2+} ions in the octahedral layer and subsequent release of hydroxy ions coordinated to magnesium. This can be expressed as:

$$Mg(OH)_2 \Longleftrightarrow Mg^{2+} + 2OH^- \tag{1}$$

It should be noted that while the Mg concentration in sepiolite suspensions at natural pH is about 3.1×10^{-4} mol/l, that at pH 2 is 2×10^{-2} mol/l, as shown in Fig. 2.

It is due to this fast dissolution that sepiolite suspensions require continuous pH adjustment particularly in the acidic pH. Figure 1 also illustrates that when the suspension pH is adjusted to 11, it comes down to 9.5 after 30 min. and to its equilibrium pH only after several hours. The decrease in pH from 11 to 8.5 occurs because the Si ion given in Eq. (2) reacts with the crystal water to form hydrolysis products and the resultant release of H^+ ions to neutralize OH^- ions in the basic pH. The pH decrease can be also ascribed to dissolution of tetrahedral silica in alkaline solution to form aqueous H_4SiO_4 species. The reduction of pH from 11 to 8.5 in a period of 3.5 h confirms the relatively slow nature of hydrolysis reactions (18, 19).

$$Si^{4+} + 4H_2O \Longleftrightarrow Si(OH)_4 + 4H^+ \tag{2}$$

Another reason could be the presence of Fe^{3+} in the octahedral (20) and Al^{3+} in the tetrahedral layers and the resultant release of H^+ ion into the

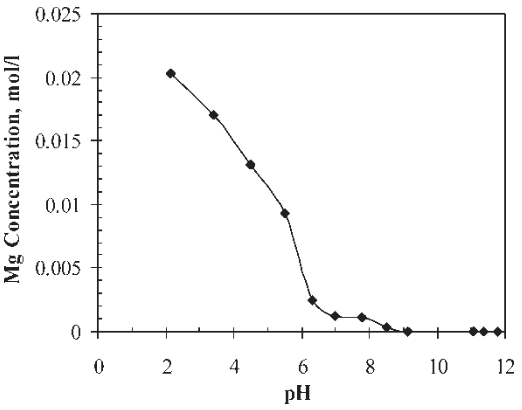

Figure 2. Variation of released Mg^{2+} concentration against pH in water-sepiolite (K4 sample) system.

system upon their hydration; this ultimately reduces the pH of the medium as follows:

$$Fe^3 + 3H_2O \Leftrightarrow Fe(OH)_3 + 3H^+ \text{and } Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3 + 3H^+ \qquad (3)$$

In both cases, H^+ ions are released into the system and neutralize the pH of the suspension.

Zeta Potential-pH Profiles and Isoelectric Point

The zp-pH profiles of sepiolite at different solids concentrations, i.e. the amount of the sample in 100 ml water are presented in Fig. 3. Zeta potential measurements conducted as a function of solids concentration reveal significant differences. Evidently, the isoelectric point (iep) of sepiolite at 0.2, 2, 3, and 5% solids concentrations yield 3.2, 5.0, 5.6, and 6.0. Such differences can be explained on the basis of increased Mg concentration at high solids concentration. Increasing the solids concentration from 0.2 to 5% proportionally shifts the zp values from negative to more positive values; this behavior was also found in the case of colemanite ($Ca_2B_5O_{11} \cdot 5H_2O$), which yielded an iep of 8.5 at 0.1% solids concentration and 10.5 at 1% solids concentration (21). Solids concentration in salt type minerals such as colemanite and calcite is known to affect the rate of mineral dissolution which is directly controlling the time required to reach equilibrium. For a given conditioning time and solids concentration, no shift in the shear plane is expected; the effect of solids concentration can be minimized by increasing the time of conditioning.

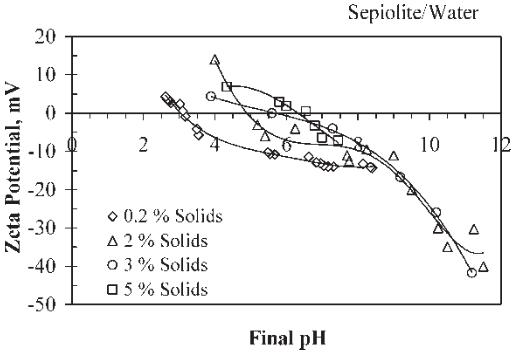

Figure 3. Variation of zeta potential of brown sepiolite (K4 sample) with pH at different solids concentrations.

Variation of zp with solids concentration and more importantly its strong buffer feature of sepiolite require that additional care be exercised. A recent study on the iep of α-sepiolite (Meerschaum) reported a value around 6 (14). Different iep values obtained for different solids concentrations point out inconsistencies in the values reported in the literature for some mineral systems.

Zeta potential measurements of sepiolite against pH at different solids concentration presented in Fig. 3 reflect the addition of acids or bases used to adjust the pH of the solution. The addition of HCl lowers the pH values resulting in an increase in the H^+ ion concentration in the solution. The adsorption of H^+ ions on sepiolite particles increases the positive charge on the mineral leading to higher zp values. On the other hand, the addition of NaOH increases the pH of the solution and leads to subsequent adsorption of OH^- ions at the sepiolite-water interface resulting in higher negative zp values. Consequently, the results are in agreement with the electrical double layer (edl) theory. It is well-known that the potential determining ions (pdi) for most clay minerals including sepiolite are H^+ and OH^- ions.

Figure 4 illustrates the zp profiles of different sepiolites from Sivrihisar-Turkey and a commercial sample (Pangel S15) from Tolsa-Spain. The iep of samples varies in the range of 3.7 to 6.0 with the lowest being Pangel S15 and the highest the brown sepiolite. Although most clay minerals and even silicate minerals have iep values around pH 2, sepiolite exhibits rather high iep values (22). An examination of Fig. 4 and Table 1 reveals that the higher MgO content correlates with the higher the iep values. There is no apparent correlation between the iep and CaO or Loss on Ignition (LOI) values.

Effect of Monovalent Ions on Zeta Potential of Sepiolite

The zeta potential behavior of sepiolite in the presence of monovalent ions is shown in Fig. 5. An examination of Fig. 5 indicates that there is an order of

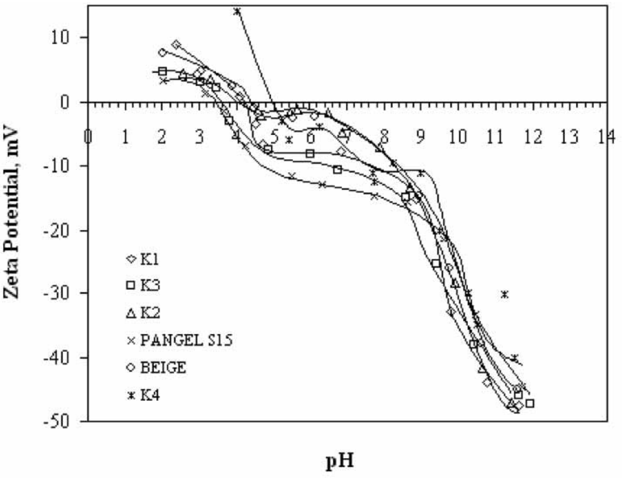

Figure 4. Variation of zeta potential of different sepiolite samples with pH (2% solids by wt.).

effectiveness particularly in the second region; this is found to follow the order of electronegativity of the ions in the order of H(2.2) > Li(1.0) > Na(0.9) > K(0.8) > Cs(0.7) (23). Irrespective of the ionic size, the ability of ions to be incorporated in the EDL and their ion exchange favors the ions of lower

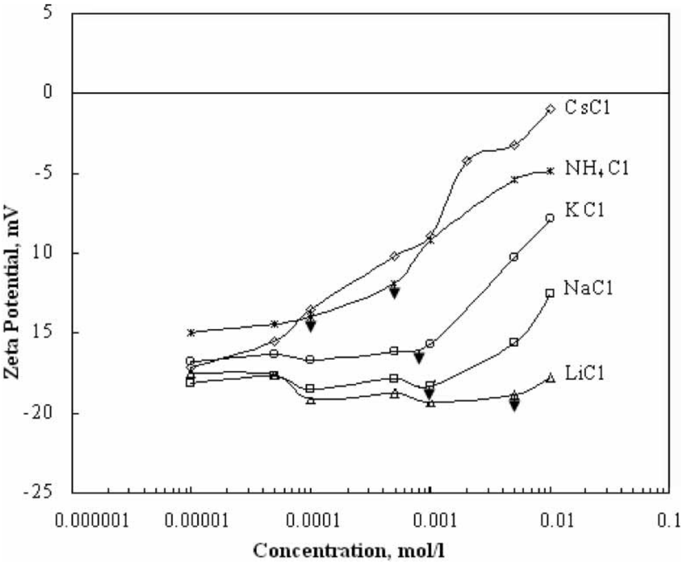

Figure 5. Effect of monovalent ions on zeta potential of K4 sepiolite. Arrows point out the offset of ion exchange.

Table 2. Size and electronegativity of various relevant ions

	Li^+	Na^+	K^+	NH_4^+	Cs^+	Mg^{2+}
Crystal radius, Å	0.6	0.95	1.33	1.44	1.69	0.65
Hydrated radius, Å	3.82	3.58	3.31	3.31	3.29	4.28
Electronegativity	1.0	0.9	0.8	—	0.7	1.2

electronegativity (Table 2). Accordingly, the exchange of Cs^+ ions with Mg^{2+} in the octahedral layer is attained until 10^{-4} mol/l ion concentration. Similarly, Li^+ ion with its highest electronegativity exhibits ion exchange over a wide range of ion concentration and remains negatively charged in the entire ion concentration.

Zeta potential behavior of minerals in the presence of added monovalent salt such as NaCl can undergo three possible modes:

a. reduction of positive charges upon electrolyte addition through adsorption of ions in the EDL and its consequent compression,
b. flat type zeta potential profile indicating exchange of monovalent ions with those in the solid to maintain electrical neutrality until ion exchange ceases,
c. increase of negative charges on addition of electrolyte due to exchange of monovalent ions and resultant release of higher valency ions in excess of electrical neutrality leaving a negatively charged deficit surface (22).

The zp curves in Fig. 5 are characterized by two regions of different slopes. The first region is dominated by ion exchange reaction between the added monovalent ion and magnesium ions in the octahedral layer. The slope remains virtually horizontal indicating that the electroneutrality is maintained. The second region is represented by double layer compression indicative of adsorption of monovalent ions in the EDL.

In order to identify the contribution of adsorption types, i.e. ion exchange and adsorption in the EDL, a series of systematic adsorption tests in sepiolite/monovalent ions were conducted and the results are given in Fig. 6. As a measurement approach, the released Mg ion concentration which identifies the magnitude of ion exchange was analyzed. The earlier suggested order is again prevalent in adsorption measurements; this indicates the influence of electronegativity of ions in this particular system. At low ion concentrations, the largest ion (Cs^+) with the lowest electronegativity undergoes ion exchange with Mg^{+2} at a higher level whereas the smallest Li^+ ion requires a wider range of concentration to attain the same level of exchange. Further research is required to identify if factors other than electronegativity such as cation solvation energy and the structure-making and breaking-tendency of cations play a role in this phenomenon.

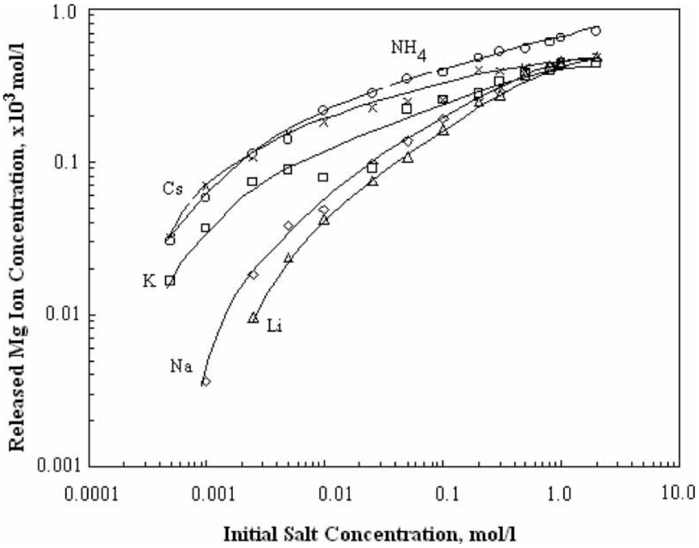

Figure 6. Released Mg^{2+} ion concentration from sepiolite matrix (K4 sample) upon addition of different monovalent salts.

Subtraction of the adsorbed amount through ion exchange from the total adsorption yields adsorption in the EDL as

$$\Gamma_{\text{Total}} = \Gamma_{\text{Adsorption in EDL}} + \Gamma_{\text{Ion exchange}} \tag{4}$$

The contribution of each mechanism is presented in Fig. 7. Although the onset of ion exchange with Na occurs at higher concentrations (1.5×10^{-3} M), over 90% of Na ions are able to exchange with Mg ions in the octahedral layer of sepiolite. Conversely, ion adsorption in the EDL is completed at relatively lower concentrations compared to the other ions. Because the clays were not Mg-saturated prior to the treatment, another plausible explanation for the released Mg may be attributed to the dissolution of sepiolite and dolomite; this may imply that structural Mg in the octahedral sheet is exchangeable whereas structural Mg is not exchangeable. Table 1 also shows the CEC values of sepiolite ranging from 16.4 to 25.6 meq/100 g whereas montmorillonites are typically reported to have CEC values of 81–124 meq/100 g (24); this clearly shows that sepiolite has some ability to undergo ion exchange.

Ion exchange with all the other three ions, i.e. Li, NH_4, and K, is initiated at low concentrations (3×10^{-4} M) but is diverted upon increasing the ion concentrations. Li apparently undergoes the highest level of ion exchange at lower concentrations. These results are in agreement with the zeta potential results in Fig. 5 where Li shows the flattest curve with highest negative zp values. The total adsorption follows the order of $NH_4 > Li > K > Na$ whereas the ion exchange shows the order of $NH_4 > K > Na > Li$.

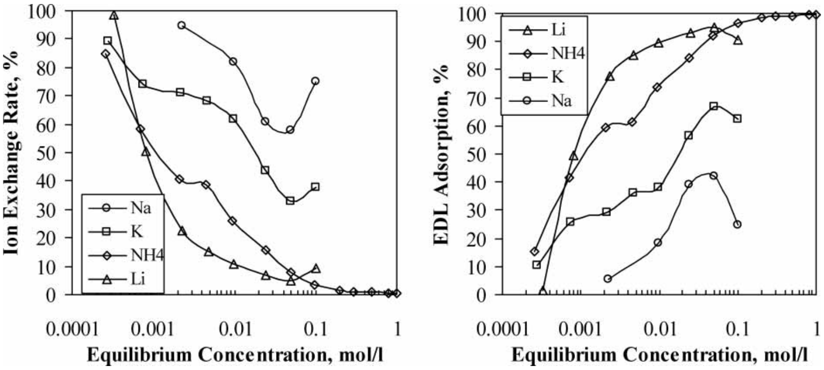

Figure 7. Adsorption of monovalent salts onto K4 sepiolite through (a) ion exchange and (b) incorporation of ions in the EDL.

A schematic illustration of monovalent ion adsorption at sepiolite/water interface is presented in Fig. 8. It is the extent and contribution of each ion to adsorption as a function of ion concentration that determines the zp profiles shown in Fig. 5. Accordingly, the order of Cs $>$ NH_4 $\gg$ K $>$ Na $>$ Li is realized. Apparently, while Cs undergoes the highest ion exchange with increasing ion concentration, Li exhibits the lowest level but gradual ion exchange; they all converge around 0.5 mol/l ion concentration. Because Li induces the most negative charge on sepiolite, it must have the least ability to get incorporated in the EDL. In summary, the combination of ion exchange and EDL adsorption determines the magnitude of the surface charge of sepiolite in the presence of monovalent ions.

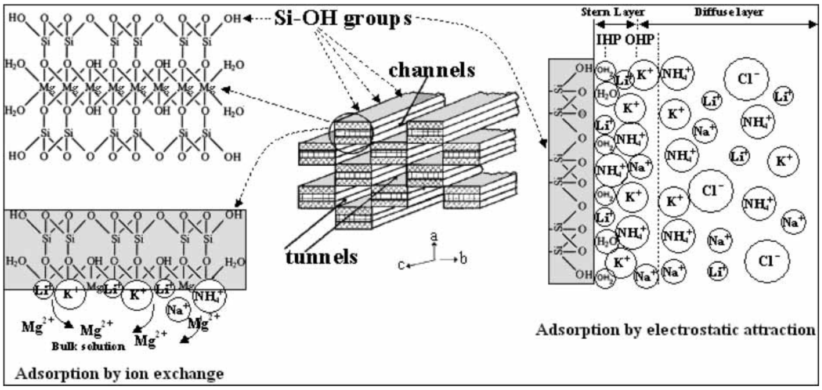

Figure 8. Proposed schematic mechanism of monovalent ion adsorption at the sepiolite/water interface.

CONCLUSIONS

1. Changing the solids concentration from 0.2% to 5% shifts the iep of sepiolite from 3.2 to 6.0, respectively. This indicates that iep values reported in the literature must be taken in caution if dilute suspensions have been used.
2. The iep of sepiolite from various deposits vary in the range of 3.7 to 6.0. Although the trend is not definitive, the higher MgO content appears to correlate with the higher iep values.
3. The relative order in which these ions reduce the zp of sepiolite with increasing concentration is $Cs > NH_4 > K > Na > Li$, reflecting the electronegativity of the cation. This order is controlled by the combination of ion exchange and the incorporation of ions in the EDL. Accordingly, because NH_4 undergoes the highest ion exchange and also highest total adsorption, it also exhibits relatively the lowest positive zeta potentials.

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