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Applying zeta potential measurements to characterize the adsorption on montmorillonite of organic cations as monomers, micelles, or polymers

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ABSTRACT

A systematic study was carried out to characterize the adsorption of organic cations as monomers, micelles, or polymers on montmorillonite by monitoring zeta potential (ζ) as a function of cation loading on the clay. In general, the clay's ζ became less negative as cation loading increased. A fairly good linear correlation between adsorption of organic cations on the clay, up to the cation exchange capacity (CEC) of the clay, and ζ potential of the composites was fitted. However, when the adsorption of the larger cation exceeded the CEC, a nonlinear increase in ζ was measured. The degree of this increase corresponds to the cation size and affinity to the clay (in the order surfactant < dye dimer < micelle). In contrast to the organic cations, ζ reached zero at polycation loadings that were significantly lower than the CEC. The zeta-adsorption plot of the polycations reached a well-defined plateau which correlates to the zeta potential of the polycations. The effect of electrolytes on ζ of the crude clay was monitored, and as expected, the extent of the effect increased with valency ($\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}$) and with intrinsic cation radius ($\text{Na}^+ < \text{Cs}^+$); however, an unexpected anion effect was observed.

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1. Introduction

Montmorillonite is a smectite clay mineral composed of one octahedral layer between two silicon-oxide tetrahedral layers. Particle size is small, 0.01–1 μm , with a high specific surface area, 700–800 m^2/g , and a cation exchange capacity (CEC) of 80–100 $\text{meq}/100 \text{ g}$ [1,2]. Adsorption on montmorillonite has been of interest for centuries due to the clay's high CEC, surface area, and swelling properties. Thus, numerous studies have been performed on interactions at the clay surface [3–8]. In addition to its superior surface properties, montmorillonite is widely used in a variety of industrial applications due to its low cost and low toxicity [9–14].

Montmorillonite is not only applied as a crude clay, but also very often as an organo-clay (also referred to as clay composite)—clays in which the inorganic cations are exchanged with organic ones to modify surface area. The adsorption of the organic cation on the clay is usually determined by direct measurement of cation loading (chemical analysis), or by measuring the concentration of the organic cation in the supernatant and calculating the amount adsorbed. Upon adsorption of organic cations, the surface charge is reduced (less negative) and in many cases, charge reversal is achieved. Therefore, cation adsorption can be monitored by measuring the change in

zeta potential (ζ) of the clay surface, a measurement which is relatively simple, rapid, and inexpensive and also provides information on the organo-clays' stability in dispersion.

Indeed ζ , the potential between the slipping plane and the bulk solution, is an important electrokinetic property of clay minerals, which has traditionally been applied to measure the stability of clay dispersions [15–18] and to characterize clay aggregation, flow, sedimentation, and filtration [19–23]. In addition to indicating colloid stability, ζ measurements play a significant role in understanding the adsorption mechanism of inorganic and organic molecules at the solid/solution interface.

In the past few decades, ζ of clays has been monitored to study the effects of the chemical properties of the bulk solution, such as pH and electrolytes, on the clay surface [20,21,24,25]. These studies have shown that divalent cations decrease the clay's ζ to a higher degree than monovalent cations [20,21,25] as predicted by the DLVO theory. The effect of heavy metals on ζ has also been investigated to develop a model for the adsorption of heavy metals on magnetite [26]. More recently, ζ measurements have been applied to study the adsorption of organic cations and polycations on clay [27–34]. In many cases, the adsorption of the organic cation exceeded the clay's CEC and the expected charge reversal was verified by ζ measurements [27,30,34]. In contrast to measurements of ζ close to zero for cation adsorption equivalent to the CEC, ζ measurements close to zero were obtained for highly charged polycations at polymer loading significantly lower than the loading required to neutralize the clay surface. This outcome was explained in terms of polycation screening the clay surface [31].

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The number of experimental studies presenting cation adsorption on clays and the consequent changes in zeta potential of the clay is increasing. However, in all of the above described studies, ζ was measured for individual cases, such as the effect of electrolytes, specific cation adsorption, and more recently, polycation adsorption. The question of whether monitoring ζ can be applied to predict adsorption on surfaces has not been conclusively answered. This study attempts to demonstrate a correlation between the type of adsorbate and its effect on ζ of montmorillonite. We present a comprehensive and systematic study in which we characterize the adsorption of organic cations as monomers, micelles, and polymers on montmorillonite and monitor ζ as a function of cation loading on the clay. In addition, we report the effect of electrolytes on nontreated montmorillonite ζ .

2. Materials and methods

2.1. Materials

Wyoming Na-montmorillonite SWy-2 clay with a CEC of 0.76 mmol/g was purchased from the Source Clays Repository of the Clay Mineral Society (Columbia, MO). Poly(diallyldimethylammonium chloride) (PDADMAC; MW 400–500 K), PDADMAC-copolyacrylamide (PDADMACcoPAM; 1/1 monomer, MW 250 K), octadecyltrimethylammonium bromide (ODTMA), hexadecyltrimethylammonium chloride (HDTMA), phenyltrimethylammonium chloride (PTMA), and benzyltriethylammonium chloride (BTEA) were purchased from Sigma–Aldrich (Steinheim, Germany). Crystal violet (CV) was purchased as chloride salt from Fluka Chemie AG (Buchs, Switzerland). All salts (NaCl, CsCl, CaCl₂, MgCl₂, and AlCl₃) were of analytical grade, purchased from Sigma–Aldrich. Structural formulas of the polymers and organic cations are shown in Fig. 1.

2.2. Methods

2.2.1. Adsorption of organic cations on montmorillonite

Organo-clays were prepared by adding the organic cations (0–200 mM) PTMA, BTEA, ODTMA, HDTMA, or CV to a montmoril-

lonite dispersion (1.67 g/L final) in centrifuge tubes. The dispersions were agitated on a shaker for 24 h (1 week for CV) to reach equilibrium [35–38], and the precipitates were then separated out by centrifugation (15,000g for 20 min) and freeze-dried. The percentage of carbon in the precipitates was measured using a CHNSO analyzer (Fisons, EA 1108, Waltham, MA, USA), and the amount of cation adsorbed calculated for PTMA, BTEA, ODTMA, and HDTMA. The concentration of CV in the supernatant was measured by a UV–Vis spectrophotometer (Thermo Scientific, Evolution 300, Waltham, MA, USA) and the adsorbed concentration was calculated.

2.2.2. Adsorption of polycations on montmorillonite

Solutions (8 mL) of PDADMAC or PDADMACcoPAM (0–20 g/L, final concentration) were added to a clay dispersion (4 mL) of montmorillonite (1.67 g/L, final concentration). Dispersions were kept under agitation for 2 h (to reach equilibrium [31]) and then centrifuged (15,000g for 20 min). The precipitates were freeze-dried and the percentage of carbon was measured using a CHNSO analyzer. The amount of polymer adsorbed was calculated according to the percentage carbon in the composite.

2.2.3. Effect of electrolytes on zeta potential of montmorillonite

Montmorillonite was dispersed (1.7 g/L) in salt solutions of NaCl, CsCl, CaCl₂, or AlCl₃ at concentrations of 0–100 meq/L. ζ of the dispersion was measured following 24 h agitation on a shaker.

All the experiments were preformed at temperature of 25 ± 1 °C.

2.2.4. Zeta potential measurements of the composites

The organic- and polymer-clay composites were redispersed at a concentration of 1.7 g/L. The samples were allowed to settle for approximately 1 h and a few milliliters of dispersion from the top of the tube was measured. The temperature of the samples was 25 ± 1 °C. ζ was measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA), where the ζ was deduced from the mobility of the particles using the Smoluchowski equation.

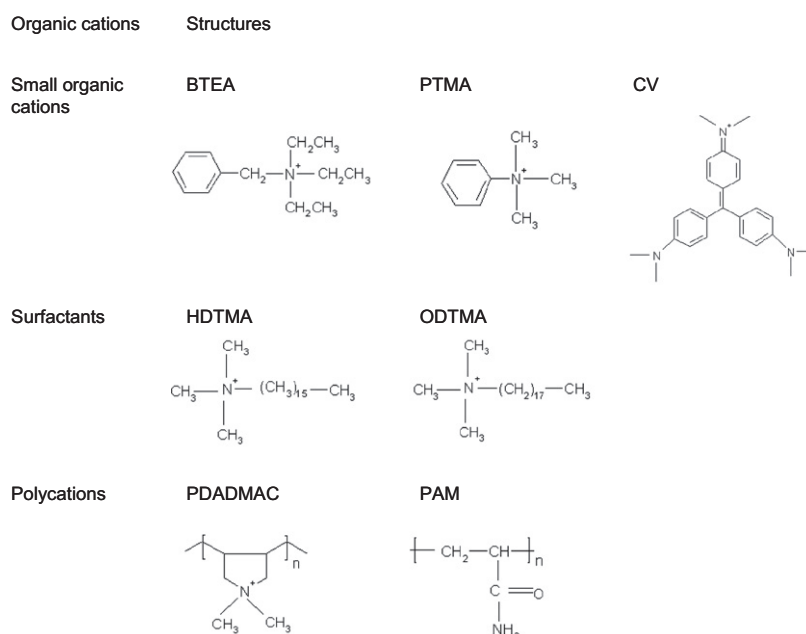


Fig. 1. Molecular structures of the organic cations.

3. Results and discussion

3.1. Effect of Na-montmorillonite concentration on zeta potential

ζ values of Na-montmorillonite dispersions in distilled water were not significantly affected by clay concentration in the range of 0.05–0.3 wt.%. For a clay concentration of 0.5 g/L, the measured ζ was -37 mV. This value increased slightly with clay concentration (1 g/L) to -42 mV, but remained constant up to a concentration of 3 g/L. In this study, the clay samples (1.7 g/L) were allowed to settle for approximately 1 h and a few milliliters from the top of the dispersion was measured, giving an average ζ of -43 ± 4 mV. The error in ζ was larger at values close to zero, reaching ± 10 mV.

3.2. Adsorption of organic cations on montmorillonite and zeta potential of the composites

The change in ζ of Na-montmorillonite as a function of the amount of organic cation adsorbed on the clay was monitored. We selected five common organic cations in which their adsorption (as monomers or micelle) to clay minerals has been widely studied: two small aromatic quaternary ammonium cations (PTMA and BTEA), two cationic quaternary ammonium surfactants (ODTMA and HDTMA), and the dye CV. PTMA adsorption did not reach the clay's CEC (0.76 mmol/g), even when the initial organic cation concentration was 150% of the CEC. BTEA adsorption reached the CEC but did not exceed it. These adsorption results are in agreement with previous studies [35,37]. The adsorption of ODTMA and HDTMA at concentrations below their critical micelle concentration (CMC) (i.e., as monomers) was complete for added concentrations between 0% and 100% of the CEC of the clay. At added concentrations above the clay's CEC, ODTMA adsorption (as mono-

mers) decreased slightly (90.5% adsorption), while the decrease in the adsorption of HDTMA was more pronounced (73.6% adsorption), indicating that ODTMA has a higher affinity to the clay than HDTMA due to its longer alkyl chain. Similar results have been reported by Mishaal et al. [36]. The adsorption of ODTMA added at concentrations above the CMC (i.e., as micelles) on montmorillonite was complete, even at high initial organic cation concentrations reaching adsorption of 150% of the CEC. Complete adsorption of ODTMA micelles by montmorillonite has been previously shown [39,40].

Adsorption of organic cations above the clay's CEC has been widely reported and discussed. Cation adsorption below the CEC is mainly due to electrostatic interactions and adsorption above the CEC to additional hydrophobic interactions between the adsorbing cations [27,30].

The measured values of ζ as a function of PTMA, BTEA, HDTMA, ODTMA, and CV adsorption on Na-montmorillonite (% of CEC adsorbed) are presented in Fig. 2A. ζ of the composites reflected the adsorption isotherms of all cations studied, i.e., ζ was less negative with an increase in cation loading and was positive for composites in which cation adsorption was above the CEC. For example, ζ of PTMA and BTEA reached, at maximum adsorption, values of -14.8 ± 4.3 and -0.17 ± 0.15 mV, respectively, indicating that PTMA adsorption does not reach the CEC whereas BTEA does. The adsorption of the larger cations, HDTMA, ODTMA, and CV (at high added concentrations), exceeded the clay's CEC, correlating with the positive ζ measured for these composites. The adsorption of CV above the CEC as dimers is discussed in detail by Rytwo et al. [38].

It is difficult to establish a quantitative relationship between ζ and the amount of cation adsorbed for several reasons, such as the surface potential is higher than ζ and in the case of montmorillonite a significant part of the charges is not located at the particle

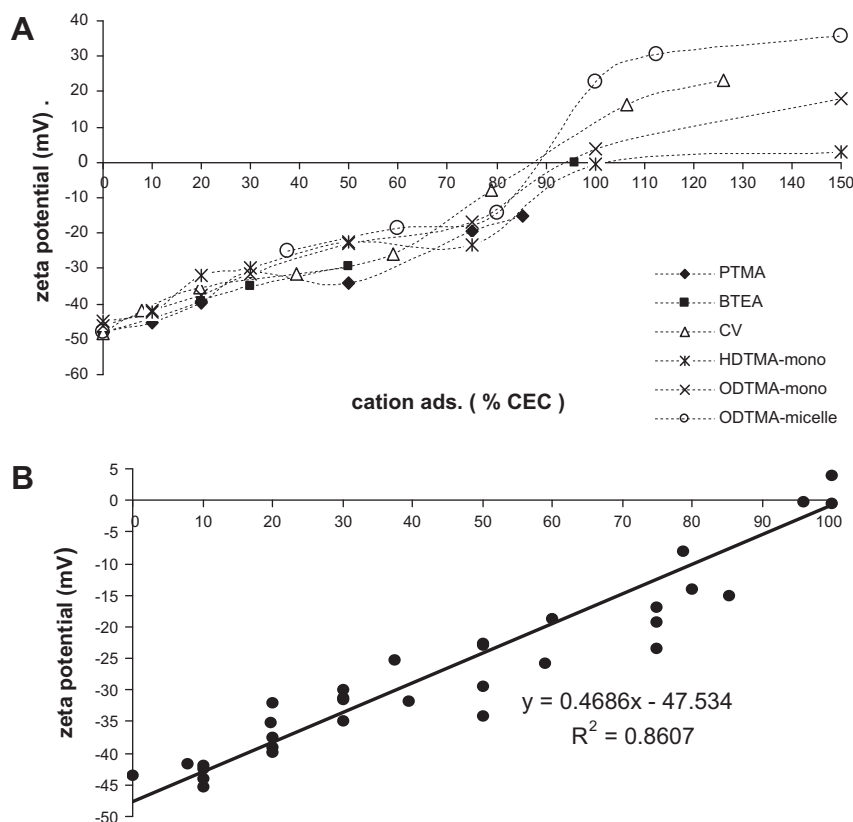


Fig. 2. (A) Zeta potential (ζ) of organic cations as a function of their adsorption on Na-montmorillonite. (B) Correlation between ζ and cation adsorption below the clay's CEC.

surface. However, when plotting ξ values as a function of cation adsorbed, at adsorbed concentrations up to the CEC, a fairly good linear correlation was fitted ($R^2 = 0.86$) where the confidence interval (95%) did not overlap (Fig. 2B). Such a relationship may enable estimating the amount of cation adsorbed by measuring ξ or vice versa estimating ξ when the amount of adsorbed cation is known.

For cation adsorption exceeding the clay's CEC, a dramatic non-linear increase in ξ was obtained. The degree of increase in ξ , upon adsorption above the CEC, corresponded to cation size, surfactant < dye dimer < micelle, and to affinity of the cations to the clay as calculated by Rytwo et al. [38] and Mishael et al. [36] based on the model developed by Nir et al. [41]. The binding coefficients calculated for HDTMA and ODTMA adsorbed as monomers and for CV were 2×10^3 , 8×10^3 , and $1 \times 10^6 \text{ M}^{-1}$, respectively. Such a correlation between size and affinity to colloids has also been reported for the adsorption of surfactants on clinoptilolite [27]. The binding coefficients of ODTMA and HDTMA as micelles were not calculated, but as demonstrated in Fig. 2, and in the adsorption isotherms of the surfactants as monomers and as micelles, the micelle configuration has a much higher affinity to the clay and reaches higher adsorption capacities [36].

The effect of the high affinity of the micelles and of CV was also demonstrated by ξ values of approximately zero, measured at cation loadings slightly lower than the CEC. This is in contrast to the cases of small organic cations and surfactants (as monomers), in which ξ values were zero for adsorption at the CEC.

3.3. Adsorption of polycations on montmorillonite and zeta potential of the composites

Two polymers with different cationicities (percentage of charged monomers which describes charge density) were selected: PDADMAC with a high charge density (100% cationicity) and PDADMACcoPAM with a 1:1 monomer ratio, i.e., 50% cationicity. The difference in cationicity was also expressed in the ξ values of the polymers: 71 ± 4.7 and $25 \pm 3.3 \text{ mV}$ for PDADMAC and for PDADMACcoPAM, respectively. Adsorption isotherms of the two polycations (0–20 g/L) on montmorillonite (1.67 g/L) are presented in Fig. 3. Adsorption of PDADMAC and the copolymer reached much higher loadings (4.5 and 13.0 mmol/g, respectively) than the organic cations. Many studies on polycation adsorption to negatively charged surfaces in general, and to clay minerals in particular, attribute the high adsorption affinity of polycations to electrostatic interactions and to the configuration of the polycation on the clay as loops and tails which enables high polymer loadings [31,42–46]. The configuration of loops and tails on the surface can also explain the higher adsorption of PDADMACcoPAM in comparison with PDADMAC. Lower charged polymers tend to adsorb more as loops and tails in a configuration extending into the solution,

resulting in a higher overall adsorption on the clay [46–50]. Although the copolymer reaches higher adsorption when polymer is added at high concentrations (above 0.5 g/L), at added polymer concentrations below the clay's CEC PDADMAC adsorption was complete, whereas, PDADMACcoPAM adsorption was not. This behavior is expressed by the crossing of the two isotherms (Fig. 3).

For both polycations at initial added concentrations exceeding the CEC, adsorption increased moderately without reaching a plateau. This constant moderate increase in polymer adsorption (not reaching a plateau) has been explained by polycation adsorption in a loops-and-tails configuration. Such a configuration enables accommodation of high polymer loadings. Shin et al. [46] suggested that as the isotherm plateau is approached, the increase in total surface mass is accompanied by a decrease in the train fraction and increase in the loops and tails fraction. Radian and Mishael [31] showed that XRD and FTIR measurements support PDADMAC adsorption on montmorillonite in a configuration of loops and tails at high polymer loadings (7.55 mmol/g).

The differences in the polycations' adsorption on the clay were reflected not only in their adsorption isotherms but also in the ξ values of the different composites. The changes in ξ potential as a function of polycation loading on the clay are displayed in Fig. 4. The ξ values of the polycation composites did not fit the linear correlation obtained for the organic cations presented in Fig. 2B. To exclude the argument that the change in ξ is due to polymer screening of the clay surface and not due to charge, the changes in ξ of montmorillonite as a function of the adsorption of a nonionic polymer, PAM, were monitored and no significant change in ξ was found.

ξ values of the polycation-clay composites were less negative with increased loading of adsorbent on the clay. Unlike the organic cations (as monomers), for which positive ξ values were measured at adsorption loadings approaching the CEC (Fig. 2A), for polycation adsorption, positive ξ values were measured for composites in which adsorption did not exceed the CEC. ξ reached zero for PDADMAC and PDADMACcoPAM composites at extrapolated loadings of 0.24 and 1 mmol/g, respectively. Taking into account only charged monomers of the copolymer, positive values of ξ were reached at a loading of 0.5 mmol/g, which is lower than the CEC (0.76 mmol/g). This pre-CEC charge reversal can be explained by screening of the clay surface by the highly charged polycations extending into the solution, even at loadings lower than stoichiometric neutralization [31]. Polymer screening of the surface also explains the lower PDADMAC loading (0.24 mmol/g) obtained for charge neutralization relative to the loading obtained for PDADMACcoPAM (0.5 mmol/g).

As noted above the ξ values of the polycation composites did not fit the linear relationship obtained for the organic cations (Fig. 2B). Nevertheless, the plots of the amount of polycation added

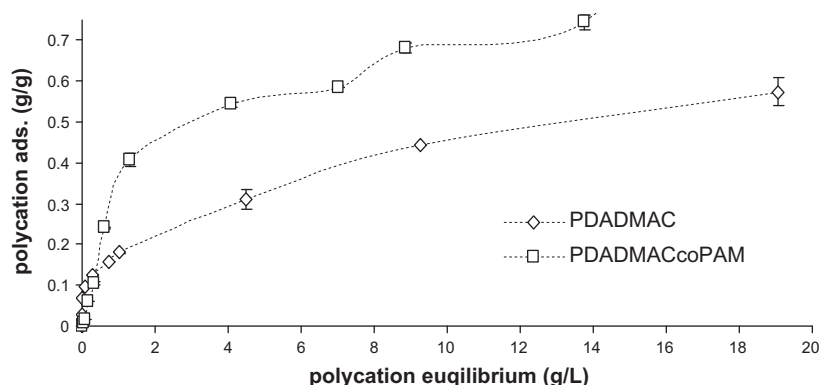


Fig. 3. Adsorption isotherms of PDADMAC and PDADMACcoPAM (0–20 g/L) on montmorillonite (1.67 g/L).

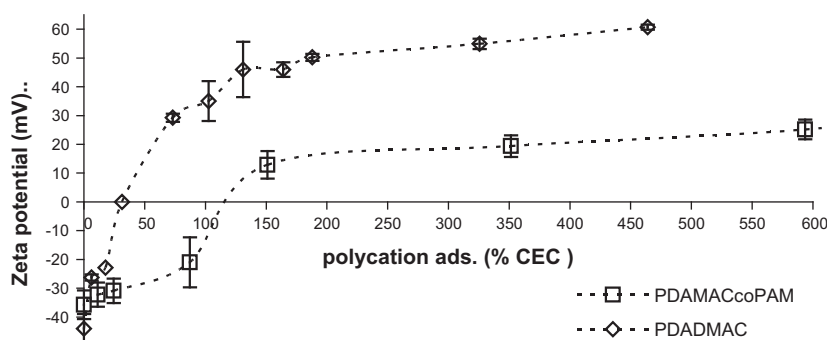


Fig. 4. Zeta potential of montmorillonite as a function of adsorbed polycation (% of the CEC).

vs. ξ of the composites (normalized to ξ of the polycations) or vs. the amount of polycation adsorbed demonstrate similar trends (Fig. 5A and B). For example, the higher affinity of PDADMAC to the clay at low concentrations (<0.5 g/L) and the higher loading reached by the copolymer at higher concentrations (>0.5 g/L) are both reflected in the plot of the added polymer vs. ξ potential (Fig. 5B).

3.4. Effect of electrolytes on zeta potential of montmorillonite

ξ of montmorillonite was monitored as a function of monovalent (NaCl and CsCl), divalent (CaCl₂), and trivalent (AlCl₃) electrolyte concentrations (0–100 meq/L) (Fig. 6). In general, ξ of the clay was less negative at high electrolyte concentrations. Increasing Na⁺, Cs⁺, and Ca²⁺ concentrations did not result in charge reversal of the clay, whereas an increase in Al³⁺ concentration did. Surface charge reversal occurred at an AlCl₃ concentration of 1×10^{-3} M, similar to the results reported by Duman and Tunç [20]. Al³⁺ adsorption, above the CEC, involved the formation of various hydroxyl complexes with the Na-montmorillonite surface, such as

Al(OH)₂⁺, Al(OH)₂²⁺, and Al(OH)₃, in the studied pH range (5.5–6.5). The degree of change in the clay's ξ increased with cation valency (Na⁺, Cs⁺ < Ca²⁺ < Al³⁺), as predicted by the double layer theory. This theory, which is the most widely used model for describing sorption behavior, derives an equation describing the ionic distribution in the diffuse layer formed adjacent to a charged surface. It predicts that increasing electrolyte concentration and valency will decrease the thickness of an electric double layer [51], which should result in a decrease in the magnitude of ξ .

It is well known that for cations with the same valency, surface affinity is related to their hydrated radius, with the smallest hydrated radius allowing the closest approach to the surface and the strongest interaction [52]. This would explain the higher ξ values obtained for montmorillonite in a CsCl solution in comparison to a NaCl solution. Furthermore, Nir et al. [41] calculated the binding coefficients of several inorganic cations to montmorillonite and found the binding coefficient of Cs⁺ to be 200-fold higher than that for Na⁺. The low binding coefficient of Na⁺ may also partially explain the high negative ξ values obtained for the clay in the presence of 100 mM NaCl (only slightly lower than those obtained for

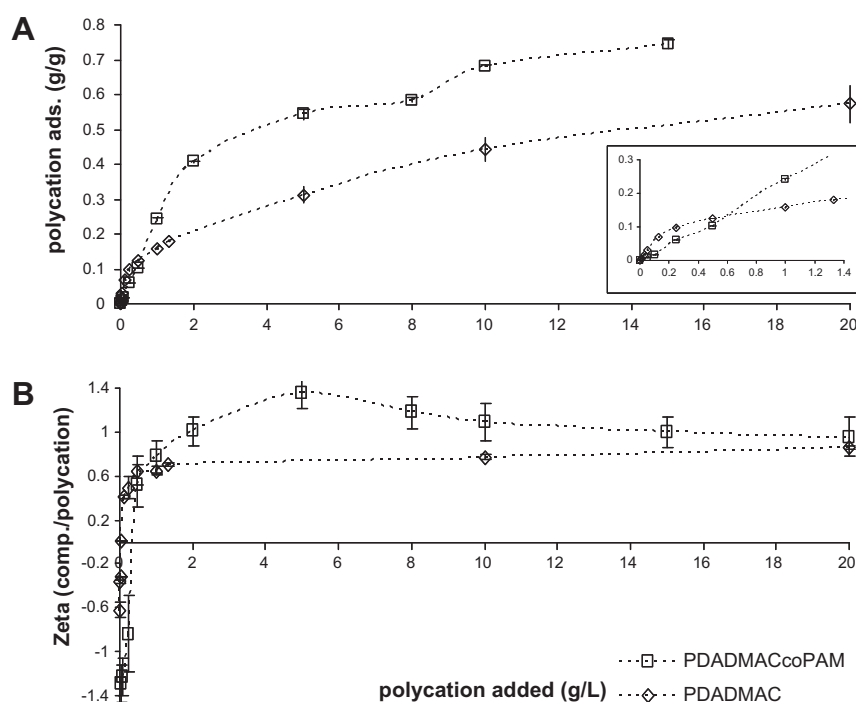


Fig. 5. (A) Adsorption of PDADMAC and PDADMACcoPAM (0–20 g/L) on montmorillonite (1.67 g/L) and (B) zeta potential of the polycation-clay composites (normalized to polycation ξ) as a function of polycation added (g/L). (Inset) Adsorption of PDADMAC and PDADMACcoPAM (0–1.4 g/L) on montmorillonite.

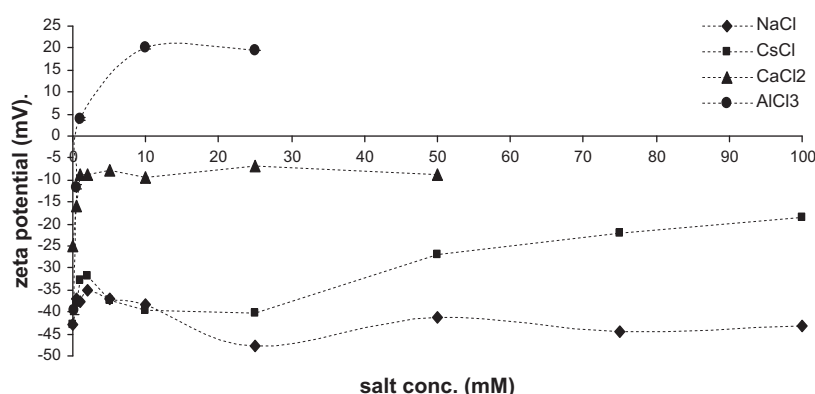


Fig. 6. Zeta potential of montmorillonite in the presence of NaCl, CsCl, CaCl₂, and AlCl₃ (0–100 mM).

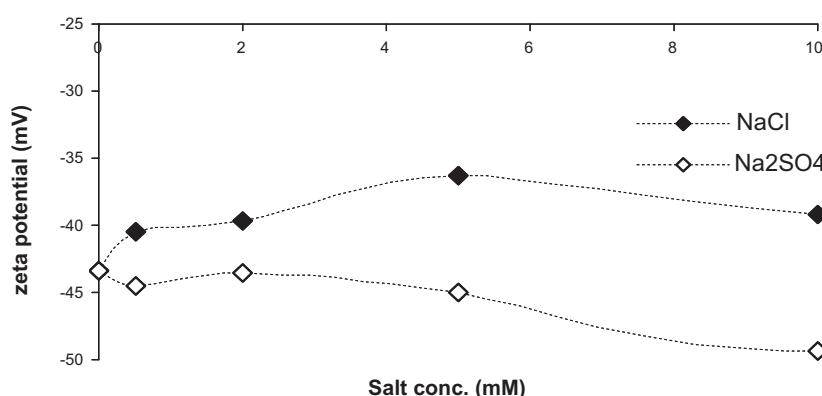


Fig. 7. Zeta potential of montmorillonite in the presence of NaCl and Na₂SO₄ (0–10 mM).

the clay with no added NaCl). Similar results have been previously reported for ζ measurement of clays in the presence of NaCl [20,53–56].

Surprisingly, the changes in ζ due to the increase in these monovalent cation concentrations were not monotonic. A sharp decrease in ζ was obtained for low electrolyte concentrations, but an increase in ζ was observed at moderate electrolyte concentrations, followed by a decrease in ζ (less negative) at higher electrolyte concentrations. The surprising increase in ζ upon the addition of moderate concentrations of monovalent electrolytes has been noted in many studies [20,53–56], but only few studies give a satisfactory explanation. Wang and Keller [21], who noted this phenomenon, suggested that the patchwise surface-charge heterogeneity includes hydrophobic patches which attract anions, resulting in an increase in ζ (more negative). In addition, a study by Elimelech and Omelia [57] showed that latex particles, which contain a significant number of hydrophobic sites, also exhibit inverted ζ behavior. This inverted behavior was explained by the entrance of co-ions (e.g., Cl[−]), as the bulk salt concentration increased, into the interfacial region adjacent to the surface hydrophobic sites, increasing the negative ζ of these particles. To examine this explanation, we measured ζ of montmorillonite as a function of Na⁺ with the divalent anion SO₄^{2−}. Indeed, a more pronounced increase in ζ was obtained when divalent anions (Na₂SO₄) approached the surface in comparison to the increase observed for NaCl (Fig. 7).

4. Conclusions

A systematic study was carried out to characterize the adsorption of organic cations as monomers, micelles, or polymers on

montmorillonite by monitoring ζ as a function of cation loading. Although it is difficult to establish a quantitative relationship between ζ and the amount of cation adsorbed, when plotting ζ values as a function of cation adsorbed, at adsorbed concentrations up to the CEC, a fairly good linear correlation was fitted. Even though the fit was obtained by six adsorption cases it may enable estimating the amount of any (small) cation adsorbed by the relatively easy measurement of ζ . For organic cation adsorption exceeding the clay's CEC, a dramatic nonlinear increase in ζ was obtained. The degree of this increase corresponds to cation size and affinity (in the order of surfactant < dye dimer < micelle for the cations examined here). In contrast to the organic cations, ζ reached zero at polycation loadings that were significantly lower than the CEC. In addition the ζ values of the polycation composites did not fit the linear relationship obtained for the organic cations. Besides characterizing clay composites, ζ measurements were applied to characterize the well-known effects of electrolytes on clay. As expected, the extent of these effects increased with valency (Na⁺ < Ca²⁺ < Al³⁺) and with intrinsic cation radius: Na⁺ < Cs⁺. An unexpected increase in ζ (more negative) was measured at moderate concentrations of these monovalent cations, which was explained by the effect of the counteranions. Finally, this study demonstrated that different types of adsorbates have different but distinct effects on ζ of montmorillonite.

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