

ADSORPTION OF POLY(VINYL ALCOHOL) ON MONTMORILLONITE

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Abstract—The adsorption of poly(vinyl alcohol) (PVA) on montmorillonites saturated with calcium (Ca-Mt) and sodium (Na-Mt) as a function of the pH value and PVA concentration in aqueous solution was studied. Owing to the binding effect of the bivalent cation, the adsorption of PVA on Ca-Mt decreases as the pH of the suspension increases, whereas adsorption on Na-Mt is unaffected by the suspension pH. The adsorption maximum of PVA (pH 6) on Ca-Mt was 151.2 mg of PVA g⁻¹ of clay, which is considerably lower than that on Na-Mt (496.2 mg g⁻¹). These adsorption data coincide with the basal spacings obtained for the clays: 1.72 and 2.26 nm for Ca-Mt and Na-Mt, respectively. Sodium permits a greater separation between the clay laminae than calcium, but in both clays the presence of the polymer gives rise to a material in which PVA is intercalated between the laminae and is also adsorbed on the external surface. Adsorption is a slow process and is irreversible in both clays.

Key Words—Adsorption, Montmorillonite, pH, Poly(vinyl alcohol).

INTRODUCTION

Water-soluble polymers are used to stabilize or to destabilize different dispersed systems and/or to change their properties such as viscosity, apparent density, specific surface, plasticity, surface energy, *etc.* Varying the relative concentration of the polymer, for example, greatly increases the viscosity of a kaolin suspension if a small quantity of PVA is added, but when increasing the amount of PVA in the clay, the viscosity decreases. This has been interpreted as due to a bridging mechanism among the microparticles and the presence of a matrix of PVA molecules (Jängström *et al.*, 1993). The study of such phenomena has important applications in several processes, for example in water clarification, mineral separation and in the soil structure (Tadros, 1978; Greenland, 1963).

Poly(vinyl alcohol) adsorption onto several materials has been studied, such as AgI (Fleer, 1971), polystyrene particles (Tadros and Vincent, 1979; Garvey *et al.*, 1975), silicon oxide (Tadros, 1974, 1978; Schulthess and Tokunaga, 1996a, 1996b), kaolin (Jängström *et al.*, 1993) and hectorite (Carrado *et al.*, 1996). Among these sorbents montmorillonite is the most common type of clay used for complex formation with polymers (Strawhecker and Manias, 2000). Adsorption of poly(vinyl alcohol) has been studied by Greenland (1963) and Emerson (1960) as a complex stabilizer of the fine particles in soils. Emerson (1960) investigated the adsorption of numerous polymers on Ca-montmorillonite, finding that PVA forms a complex with the clay, in which the polymer is not removed by certain reagents (NaCl and sodium pyrophosphate), due to the hydrogen union from

polymer OH to plate –SiO– (silanol group) of the clay. Other workers observed the same mechanism (Bajpai and Vishwakarma, 2003; Schulthess and Tokunaga, 1996a; Carrado *et al.*, 1996; Burchill *et al.*, 1983).

The formation of the PVA-montmorillonite complex will depend on the intensity of the interaction between the polymer and the smectite (Theng, 1979, 1982) and also on the exchange cation type (Carrado *et al.*, 1996). Greenland (1963) measured a greater degree of PVA adsorption on clays saturated with monovalent cations.

Our literature search for the effect of pH on PVA adsorption on montmorillonite (and the reverse) showed no results, so it is the objective of this study to determine the adsorption of PVA as a function of the pH of the system and investigate the effect of the exchangeable cation, the PVA initial concentration, the reversibility of the PVA adsorption in aqueous solution and the time taken for the reaction of PVA with montmorillonite.

MATERIALS AND METHODS

The adsorbent used in the present study is a montmorillonite from a deposit at Cerro Bandera, Neuquén, Argentina, with minor impurities of quartz, kaolinite and Fe oxide, a cation exchange capacity (CEC) of 80.2 cmol_c kg⁻¹ and a specific surface area of 808 m² g⁻¹ as determined by glycerol adsorption. Based on chemical analysis (Peinemann *et al.*, 1972), the structural formula of the studied montmorillonite is [(Si_{7.94}Al_{0.06})^{VI}(Al_{2.78}Fe_{0.40}M_{0.18}Mg_{0.64})^{VI}O₂₀(OH)₄]^{0.70-}Na_{0.70}⁺ where M³⁺ is an undetermined trivalent metal, possibly Mn.

A sample of the clay was washed repeatedly with distilled water, ultrasonically dispersed, and the <2 μm fraction separated by centrifugation. While still in suspension, the fraction was separated into two samples, one of which was washed three times with 0.5 M CaCl₂ and the other with 1 M NaCl. The excess salts were

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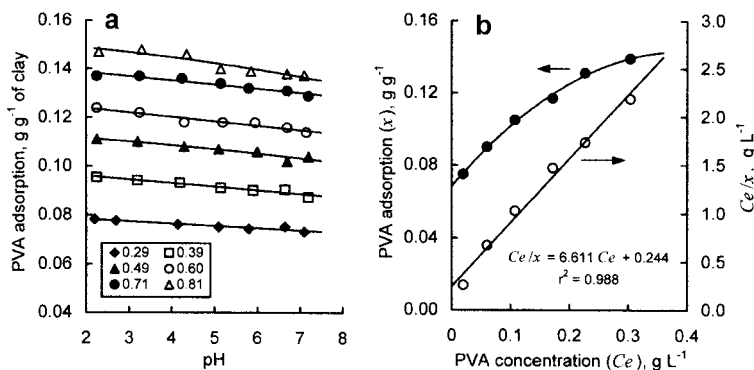


Figure 1. (a) PVA adsorption on Ca-Mt, as a function of equilibrium pH and the initial concentration of PVA (g L⁻¹). The numbers in the figure represent the initial concentrations of PVA (g L⁻¹). (b) Adsorption isotherm (at pH 6) of PVA on Ca-Mt as a function of the equilibrium concentration (●). The straight line represents the fit of the data to the Langmuir equation (○).

subsequently eliminated with de-mineralized water, first by decantation and then by dialysis in distilled water until a solution almost free of Cl⁻ (traces) was obtained. The fractions were then dried at 60°C, ground and passed through a 200 μm-mesh sieve and the water content was determined in order to express the results in dry weight at 110°C. Two homoionic clays were obtained in this way: (1) Ca-Mt with a 75 cmol_c kg⁻¹ of exchangeable Ca²⁺ (determined by exchange with Ba, using 1 M BaCl₂ at pH 5; the displaced calcium was determined by spectrophotometry). The amount of the exchangeable Ca is small, probably owing to the fact that the exchange was not complete. (2) Na-Mt with 84 cmol_c kg⁻¹ of Na⁺ (obtained by exchange with Ba). The excess Na is probably due to the presence of free Na.

The specific surface area of the clays was obtained by the orthophenanthroline (OP) adsorption method (Bussetti *et al.*, 1980): 1,10-phenanthroline [C₁₂H₈N₂·H₂O] of analytical grade, was provided by Merck (Germany).

The polyvinyl alcohol used as adsorbate (provided by BDH Chemicals Ltd., USA) was of analytical grade, had a molecular weight of 14,000 and a 98.5–100% degree of hydrolysis with a polyvinyl acetate residue of 0–3%.

To obtain the adsorption isotherms, 0.1 g samples of clay were weighed in glass Pyrex flasks with stoppers, to which were added 25 mL of solution with different PVA concentrations and pH (adjusted with HCl and/or Ca(OH)₂ and NaOH). The initial concentration of PVA ranged from 0.29 to 8.25 g L⁻¹ and the pH varied from 2 to 9 (Figures 1 and 2). The samples were shaken (300 rpm) for 1 h and then left for 18 h at 28°C under intermittent shaking, after which the pH values were determined and the samples were centrifuged. The amount of PVA in the solution was obtained colorimetrically using an iodine reagent containing 0.06 M I₂, 0.05 M KI and 0.64 M H₃BO₃, a higher concentration of KI than that given by Fleer (1971) to completely dissolve the I₂ (Kolthoff *et al.*, 1975).

All experiments were carried out in duplicate and simultaneously. The quantity of PVA adsorbed on montmorillonite was obtained from the difference between the initial and final concentrations.

An experiment was carried out to determine the reversibility of PVA adsorption as a function of contact time. Aliquots of 0.1 g of each clay were weighed in centrifuge tubes with stoppers and 25 mL of PVA solution were added. The tubes were shaken for 1 h and

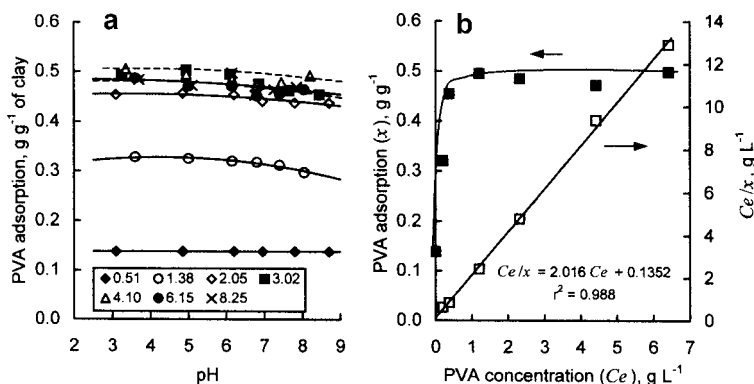


Figure 2. (a) PVA adsorption on Na-Mt as a function of equilibrium pH and the initial concentration of PVA (g L⁻¹). The numbers in the figure represent the PVA initial concentrations (g L⁻¹). (b) Adsorption isotherm (at pH 6) of PVA on Na-Mt as a function of the equilibrium concentration (■). The straight line represents the fit of the data to the Langmuir equation (□).

then left at 28°C for 7 days under daily shaking of 1 h; thereafter they were centrifuged and 12.5 mL of supernatant liquid were removed to determine the equilibrium PVA concentration. This was followed by the addition of 12.5 mL of PVA solution to the centrifuge tube such that the concentration was double that of the previous equilibrium, and the process was repeated five times. Once the desired adsorption value had been reached after a contact time of 35 days in total, the tubes were centrifuged and 12.5 mL of the PVA solution were removed to determine their concentration, 12.5 mL of distilled water were added to the centrifuge tube to reduce the PVA concentration by half, and the tube was shaken for 1 h and then left at 28°C for 7 days under daily shaking. The samples were centrifuged thereafter and 12.5 mL of the supernatant were removed to determine the equilibrium PVA concentration. A further 12.5 mL of distilled water were added to reduce the PVA equilibrium concentration by half, and the whole process was repeated four times (35 days). The initial concentrations (C_i) for each sample were: Ca-Mt, $C_i = 0.31-0.75$ g PVA L⁻¹ and Na-Mt, $C_i = 0.52-3.78$ g PVA L⁻¹.

Statistical analysis of the experimental data was performed with one-way ANOVA, with the quantity of OP adsorbed as the dependent variable and the pH, initial and final concentrations parameters as the independent variables. Comparisons between pairs of means were performed using the Student test. Statistical significance was considered at a confidence level of 95% (Snedecor and Cochran, 1980).

X-ray diffraction (XRD) analysis using Ni-filtered CuK α radiation (Rigaku-Denki Geiger Flex model D Max 3C diffractometer) was carried out on samples of Ca-Mt and Na-Mt and on samples from the experiments on PVA adsorption. Clay suspensions in water (4% weight/volume) with and without PVA were prepared; 4 mL were placed on glass disks, and evaporation was allowed to take place at room temperature inside a desiccator with silica gel. In this way, very fine homogeneous laminae with naturally oriented particles were formed.

RESULTS AND DISCUSSION

Specific surface area of Ca- and Na-montmorillonite

The maximum adsorbed quantity of OP (determined by the linear Langmuir equation) at pH 6 was 1.70 and

2.06 mmol g⁻¹ for Ca-Mt and Na-Mt, respectively, giving specific surface areas of 614.2 m² g⁻¹ and 744.3 m² g⁻¹, respectively (Table 1) (OP molecules cover a surface area of 361.3 m² mmol⁻¹; Bussetti *et al.*, 1980).

Numerous adsorbates have been used to determine the specific surface areas of different minerals, the resulting surface area depending on the size of the adsorbate and the surface energy of the adsorbent (Ferreiro *et al.*, 2002; Helmy *et al.*, 1998, 1999a, 1999b). We have used the OP adsorption method proposed by Lawrie (1961), improved by Bower (1963) and studied thoroughly by Bussetti *et al.* (1980). It was found that fewer OP molecules are adsorbed onto montmorillonite when the exchange charge is saturated with a bivalent cation (Ca²⁺) than when it is saturated with a monovalent cation (Na⁺). This is the reason why the clays show different surface areas when determined by OP adsorption.

Adsorption of PVA on Ca- and Na-montmorillonite

Statistical analysis of the duplicates of the adsorption experiments demonstrated that in the system Ca-Mt/PVA there are no significant pairwise differences among the means; the same was true for duplicates of Na-Mt/PVA. Figures 1a and 2a show the average PVA adsorption on Ca-Mt and Na-Mt for each initial concentration of the polymer and as a function of the pH value of the suspension. The adsorption isotherms (Figures 1b and 2b) can be obtained from the equilibrium concentrations at pH 6, based on the adsorption values at this pH and the initial concentrations. We have taken pH 6 as a reference since it is closest to the equilibrium value of the Ca-clay suspensions in the aqueous solutions of PVA without the addition of acid and/or hydroxide. At lower pH values, exchange processes take place with the hydrogen and with the Al liberated from the clay structure; and at higher pH there is an excess of cations (Ca²⁺ or Na⁺). The amount of PVA adsorbed on Ca-Mt and/or Na-Mt as a function of the equilibrium concentration gives rise to an H-class isotherm, subgroups 1 and 2, respectively (Giles *et al.*, 1974). The H-type isotherms indicate that PVA is adsorbed in large quantities and packed densely. Bajpai and Vishwakarma (2003) found an adsorption isotherm of the 'L III category' when studying the PVA adsorption on Fuller's earth, suggesting a multilayer formation of PVA chains over the clay surfaces.

Table 1. Some characteristics of cation-saturated montmorillonites.

Material	Exchangeable cations (cmol _c kg ⁻¹)	A* (m ² g ⁻¹)	Water (%)	001 basal spacings (nm)	
				No PVA	After PVA sorption**
Ca-Mt	75	614.2	14.5	1.51	1.73
Na-Mt	84	744.3	7.5	1.26	2.26

* Specific surface area

** 151 mg PVA g⁻¹ Ca-Mt and 493 mg PVA g⁻¹ Na-Mt; water content <4%

Maximum PVA adsorption was determined through the linear form of the Langmuir equation of adsorption. Straight lines are obtained for both clays (Figures 1b and 2b) with good correlation coefficients ($r^2 = 0.988$ for Ca-Mt and $r^2 = 0.999$ for Na-Mt). The specific maximum adsorption values obtained are: 151.2 mg g^{-1} and 496.2 mg g^{-1} for Ca-Mt and Na-Mt, respectively.

These quantities of PVA adsorbed are in agreement with the increment in the basal spacing (d_{001}) to 1.73 nm for Ca-Mt and 2.26 nm for Na-Mt (Table 1), and also with the specific surface area data for each clay, 614.2 and $744.3 \text{ m}^2 \text{ g}^{-1}$ for Ca-Mt and Na-Mt, respectively, which is perfectly compatible with the location of PVA molecules between the laminae (each unit of PVA has a maximum thickness of 0.4 nm when parallel to the surface) (Fleer, 1971). In the XRD patterns for Ca-Mt (Figure 3), an increment from 1.51 to 1.73 nm can be observed in the basal spacings in the presence of PVA, and from 1.26 to 2.26 nm in Na-Mt for a larger amount of PVA adsorbed on the clay. Whereas in Ca-Mt and Na-Mt the main 001 peak reflections are well defined, indicating a very ordered structure, in the presence of PVA, the peaks for both clays show the characteristics of a moderately disordered material, indicating the presence of the PVA in the interlaminal spaces though not throughout, since if this were the case, the degree of disorder would be much greater, as shown by the XRD patterns for delaminated montmorillonite by Giannelis *et al.* (1999). The results above indicate that under these

adsorption conditions, the PVA molecules form a material intercalated with PVA in the interlaminal space and on the external surface, according to the models proposed by Carrado *et al.* (1996).

Being a bivalent cation, the Ca charge is 'shared' between the upper and lower laminae. To a certain extent this impedes further separation of the laminae ($d = 1.73 \text{ nm}$), so that for a given contact time, PVA adsorption (151.2 mg g^{-1}) is less than it would be in the presence of a monovalent cation such as Na^+ . This would indicate that at pH 6 there would be a PVA chain in the interlayer of Ca-Mt, similar to the model proposed by Carrado *et al.* (1996) for the PVA adsorption on Li-hectorite with a basal spacing of 2.04 nm .

Sodium allows a bigger separation of the clay sheets than Ca, and the basal spacing in the presence of PVA of 2.26 nm would allow the intercalation of two PVA chains in the clay with the quantity in agreement with the adsorbed amount and coinciding with the structure model proposed by Greenland (1963). The intercalated form presents the polymer molecules inserted among the sheets of the smectite, so that the interlaminal spacing is expanded, but the distance between adjacent sheets is very well defined. The clay laminae can be very separate (up to 14 nm between laminae, according to Besoain, 1985) enabling the PVA molecules to penetrate more easily and thus achieve a greater degree of adsorption (496.2 mg g^{-1}). This inter-laminar expansion is due, in general, to the presence of a monovalent cation, making

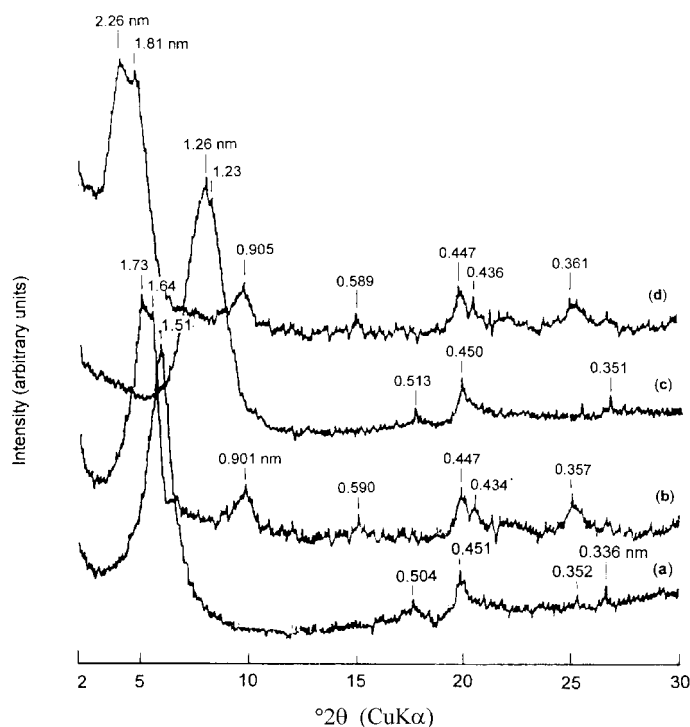


Figure 3. XRD patterns of (a) Ca-Mt, (b) Ca-Mt/PVA, (c) Na-Mt and (d) Na-Mt/PVA.

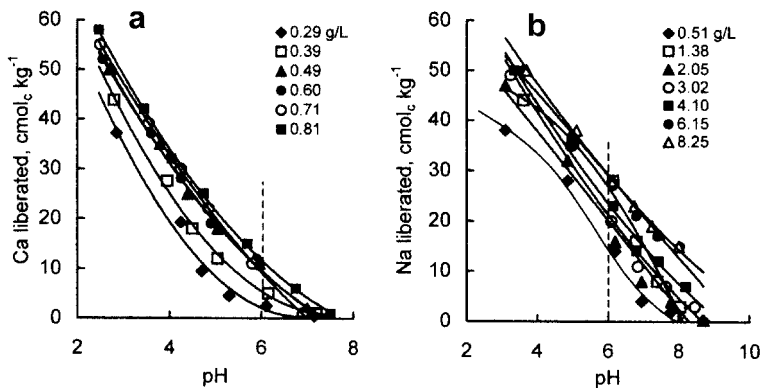


Figure 4. Ca (a) and Na (b) liberated by PVA-montmorillonites as a function of the equilibrium pH. The numbers in the figures represent the initial PVA concentrations (g L^{-1}).

PVA adsorption indifferent to the pH of the suspension (Figure 2a) within the range studied; to reach pH values of between 2 and 9. This is in agreement with the fact that montmorillonite can form a wide range of complexes, exhibiting an indefinite dimension with some monovalent cations (MacEwan, 1961).

In Figure 4 a greater liberation of Ca and/or Na takes place when the pH decreases and the initial PVA concentration in the solution increases. At smaller pH values, some Ca ions are liberated from the surface by exchange with H^+ (Figure 4). Hydrolysis also takes place on the smectite crystals with the partial liberation of Al that would also replace the exchange cation. At pH 6, for any initial PVA concentration, the quantity of Ca in the solution ($2\text{--}12 \text{ cmolc kg}^{-1}$) is much smaller than that of Na ($12\text{--}28 \text{ cmolc kg}^{-1}$), due mainly to a phenomenon of selectivity of the Ca and/or Na cations before H^+ . The liberation of the cations affects Ca-Mt/PVA more, since, when displacing the surface Ca^{2+} for a monovalent cation (H^+), the smectite sheets can separate more. This is the reason why only a slight increase in adsorption is observed upon lowering the pH (at pH 2.5, maximum PVA adsorption is 155.3 mg g^{-1}) and increasing the initial PVA concentration (Figure 1a). A change is not observed in the PVA adsorption on Na-Mt due to the exchange of Na^+ for H^+ (Figure 1b).

Irreversibility of PVA adsorption on Ca- and Na-montmorillonite

The Student's test did not show any significant differences between the duplicates of experimental data in either adsorption-desorption system (Ca-Mt/PVA, Na-Mt/PVA). The results of the adsorption-desorption process after a period of 7 days are shown in Figure 5. In both the Ca- (Figure 3a) and Na-clays (Figure 3b), the process of adsorption is irreversible, as demonstrated by the line representing the quantities of PVA desorbed over a period of 7 days. Although adsorption increases as a function of contact time with both clays, such increase is more marked for Ca-Mt, indicating that in this material the adsorption reaction continues despite a 50% decrease in the equilibrium concentration of PVA. Only four dilutions are required in order to reach a final PVA concentration close to zero and an adsorption of 160 mg g^{-1} , greater than the initial adsorption of 131 mg g^{-1} . Since Na-Mt is more dispersed and, for the reasons given above, reaches a higher initial level of adsorption (515 mg g^{-1}), in the case of this clay five dilutions are required in order to reach a PVA concentration close to zero and obtain a final PVA adsorption of 520 mg g^{-1} . In both materials, at the end of the desorption process at almost complete dilution of the equilibrium concentration, adsorption tends towards

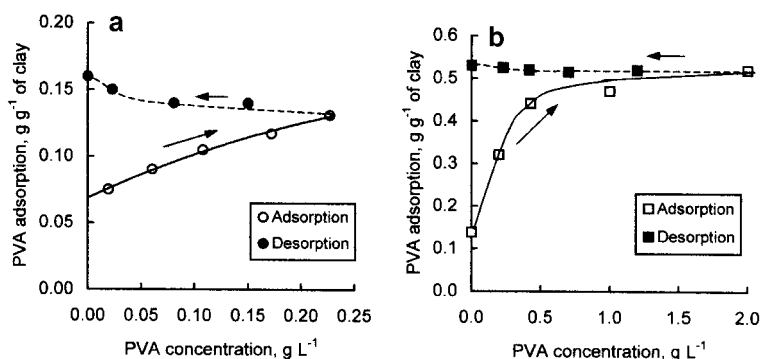


Figure 5. (a) PVA adsorption and desorption on Ca-Mt at pH 6, in periods of 7 days, as a function of the PVA equilibrium concentration. (b) The same as (a) but for Na-Mt.

the maximum value obtained for a much shorter contact time in accordance with Langmuir equation (Figures 1b and 2b). These increases in PVA adsorption may be due to the non-equilibrium effect of the PVA solution with the quantity of clay present in the suspension; to the wider dispersion of the clay particles as a result of the additional shaking of the suspensions, exposing a larger montmorillonite surface area to PVA molecules; and to a longer contact time.

Preliminary experiments demonstrated that it was not possible to remove the PVA from the clay surface by adding HCl to the suspension.

The PVA molecules appear to primarily interact with montmorillonite by H-bonding between the molecule's alcohol groups and the clay's interlaminar silanol groups ($-\text{SiO}-$) (Bajpai and Vishwakarma, 2003; Schulthess and Tokunaga, 1996a; 1996b; Emerson, 1960), which would prevent the molecules of PVA from being ejected easily from the surface by the action of chemical agents such as HCl, NaCl and sodium pyrophosphate.

CONCLUSIONS

The data on PVA adsorption by Ca-Mt and/or Na-Mt clays demonstrate that the presence of PVA molecules on the inter-laminar surface of the clays depends on the equilibrium association of the clay surfaces determined by the dominant exchangeable cation. The vinyl alcohol units behave like 'links of a chain', forming flexible elements that can adopt a variety of configurations. In this study, the H-type isotherms suggest that PVA is adsorbed in large quantities in dense packings, mainly in Na-Mt/PVA.

The PVA molecules are so strongly adsorbed onto the montmorillonite surface, independently of the exchange cation, that it is impossible to reverse the process. In the 'desorption' process, the adsorption values obtained at almost complete dilution of the equilibrium PVA concentration after 35 days, tend towards the maximum adsorption values obtained for each clay obtained from the Langmuir equation after 18 h of contact.

In both clays, a complex is formed in the presence of the polymer whereby PVA is intercalated between laminae and is also adsorbed on the external surface.

Adsorption on the Na clay is not affected by the pH, whereas adsorption on the Ca montmorillonite diminishes slightly as pH increases in the initial solution.

Under the varied conditions of initial PVA concentration, pH, cation exchange and contact time used in the present study, montmorillonite adsorbs PVA molecules, forming complexes stable for different purposes (agricultural, industrial, pharmacological, etc.).

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