

ADSORPTION OF ALKYLPHOSPHORIC ACID ON KAOLINITE AND SMECTITE IN WATER-DECANE

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Abstract—Bis-ethyl 2-hexylphosphoric acid (di-2 EHPA) dissolved in decane is chemisorbed on kaolinite and montmorillonite dispersed in an acidic aqueous solution. The adsorption results in the formation of complexes with the surface cations of the clays. The adsorption isotherms are of the Langmuir type and reveal a limiting value of adsorption on H⁺-kaolinite of 12.2 mg/g, comparable to that measured in the absence of water. For H⁺-montmorillonite, however, the limiting value in the presence of acid is somewhat less (20.6 mg/g vs. 23.8 mg/g). Di-2 EHPA does not react with the magnesium cations available at the surface. The isotherm is "stepped" and suggests the presence of adsorption sites with distinctly differentiated energies. The sites of di-2 EHPA adsorption can be masked by treating the two clay minerals with polyphosphate anions. Thus, with pyro- and tripolyphosphate anions, di-2 EHPA uptake in acidic medium is very low. Adsorbed di-2 EHPA can be recovered by treating the clays with fluoride, hydroxyl, and dihydrogenphosphate anions. Dihydrogenphosphate anions lead, however, to a state of equilibrium between the organic and inorganic phosphate anions adsorbed.

Key Words—Adsorption, Alkylphosphoric acid, Kaolinite, Montmorillonite, Phosphate polyanions, Smectite.

INTRODUCTION

Di-2 ethylhexylphosphoric acid (di-2 EHPA) is commonly used for uranium extraction in the "solvent in pulp" process in which pulped ore and an organic solvent containing an extractor are circulated countercurrently. In their study of the adsorption of di-2 EHPA on H⁺-clays in decane, Siffert and Trescol (1981) observed that the phosphoric acid group of the di-2 EHPA molecule reacted strongly in the anionic form (RO₂)₂PO₂⁻ with edge-surface cations of the clay. Adsorption of di-2 EHPA on montmorillonite and kaolinite took place at the rate of one alkylphosphate anion per surface cation, whereas adsorption on hectorite was somewhat less, taking place at the rate of two anions per three surface cations. They indicated also that adsorption of di-2 EHPA involves the formation of salts and/or surface complexes.

In an attempt to reduce the adsorption of di-2 EHPA on these clays, a study was made of di-2 EHPA adsorption in a water-decane system, under conditions that simulated those used industrially in uranium processing.

MATERIALS AND METHODS

Materials

The purification and preparation of the clay minerals used were described by Siffert and Trescol (1981). Di-2 EHPA, the organic extracting agent, which removes heavy cations by forming soluble complexes in organic phase, was tagged with P³² or C¹⁴ and used in n-decane solution, at concentrations ranging from 0.025 to 0.25

N (8.06 to 80.6 g/liter). The quantity fixed on the solid (clays) was determined by scintillation spectrometry (beta counting), using a Packard spectrometer of the PRIAS type. Because the pulp extraction of uranium is carried out under acidic conditions (pH ~ 2), H⁺-kaolinite and H⁺-montmorillonite were prepared by repeatedly treating the sodium clays with 0.03 N HCl. Protons and Al³⁺ were the exchangeable cations of the clays. Desorption of di-2 EHPA retained on the clays was carried out by stirring with dihydrogenphosphate or solutions of sodium polyphosphates in the concentration range 0.1 to 0.001 mole/liter.

Methods

A clay paste displaying the rheological properties of an industrial pulp (a highly viscous liquid) was obtained by treating 500 mg of H⁺-montmorillonite with 1.5 ml of 0.03 N sulfuric acid for 2 hr at 60°C. For H⁺-kaolinite, the proportions were 250 mg of mineral and 1.75 ml of acid solution. The final pH was 1.5 and the redox potential was 450 mV, with reference to KCl-saturated calomel electrode. Two grams of aqueous clay paste (pulp) were stirred with 10 ml of n-decane solutions of di-2 EHPA for 24 hr at 20°C and centrifuged at 15,000 rpm for 10 min. One milliliter of the centrifugate was analyzed for di-2 EHPA by beta counting. The residual clay was washed with 20 ml of distilled water. Di-2 EHPA was estimated by sampling 2 ml of this water solution. The amount of di-2 EHPA was also determined on 50 mg of clay after drying at 40°C for 48 hr. The quantity of di-2 EHPA involved was accounted for within 0.5%.

EXPERIMENTAL RESULTS

Adsorption isotherms

Figure 1 shows the isotherms for di-2 EHPA adsorption onto H⁺-kaolinite and H⁺-montmorillonite. Uptake on both minerals is lower in the presence of water than in the organic medium alone (Siffert and Trescol, 1981). Water molecules compete with di-2 EHPA for adsorption sites. Curve I is an L-type isotherm according to Giles' classification (Giles *et al.*, 1960) and yields a limiting value of 12.2 mg/g, calculated from a linear transform of the isotherm. Adsorption takes place on the edge-surface Al³⁺ at the rate of one anion per absorbing cation (Siffert and Trescol, 1981). The mechanism is an exchange of phosphate ions for Al-OH groups (Parfitt, 1978). Exchangeable Al does not seem to participate in the adsorption mechanism.

The "stepped" shape of the isotherm recorded with H⁺-montmorillonite (Curve II) suggests an adsorption on different chemical sites (Kipling, 1965; Parfitt, 1978). This differentiation of the sites was not apparent in the pure decane system (Siffert and Trescol, 1981). Two hypotheses can be proposed to explain this finding. On one hand, the Al, Fe, and Mg cations of the octahedral sheet of montmorillonite may react in succession with di-2 EHPA. On the other hand, water may favor the formation of different exchangeable groups on the Al³⁺ cations, such as Al-(OH)₂⁺ and Al-OH (Ryden *et al.*, 1977a, 1977b). If x_{m1} and x_{m2} are the uptakes corresponding to the first two plateaus, the third plateau is also a type I isotherm and, therefore, its limiting value can be calculated. The values of x_{m1} , x_{m2} , and x_{m3} are 6.35, 10.75, and 20.6 mg/g respectively. The value of x_{m3} amounts to 86% of the limiting value, $x_m = 23.8$, determined for pure decane (Siffert and Trescol, 1981). For montmorillonite (octahedral sheet composition = Al_{2.90}Fe_{0.29}Mg_{0.81}), the edge trivalent cations (Al³⁺ and Fe³⁺) represent 80% of all the cations, i.e., the adsorption sites. This value is close to the above-mentioned 86%. Magnesium cations have been probably extracted under the strongly acid conditions of the experiment and, therefore, did not participate in the di-2 EHPA uptake. This can be substantiated by indirect evidence: if various decimolar solutions of different cations are stirred with di-2 EHPA in decane at pH = 1.5, only Al³⁺ and Fe³⁺ will combine. The percentages of metal combined are: Fe³⁺ = 100%; Al³⁺ = 45%; Mg²⁺ = 0.1% (and 5% at pH = 7). From measurements on H⁺-kaolinite (whose octahedral sheets contain practically only aluminum), the limiting values of adsorption in the presence and in the absence of a water phase are roughly equal. The values x_{m1} and x_{m2} correspond to 30 and 50% occupation of the active sites, respectively. These percentages cannot be related to the cationic composition of the octahedral sheet of montmorillonite in which iron represents only 10% of the active sites.

If one rules out the interference of Mg cations during

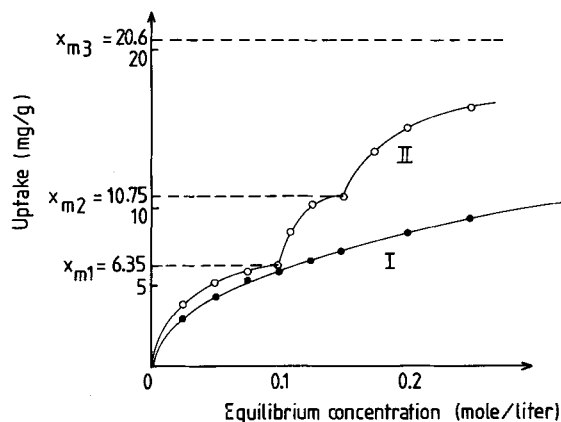


Figure 1. Adsorption isotherms of di-2 EHPA onto (I) H⁺-kaolinite; (II) H⁺-montmorillonite in decane and water.

the adsorption, the shape of the isotherm could be explained by a series of substitutions of organic phosphate anions for the -(OH)₂⁺ and -OH groups bonded to the surface Al and Fe cations. Rajan (1976), Parfitt and Atkinson (1976), and Ryden *et al.* (1977a, 1977b) explained the shape of the isotherms of phosphate adsorption by soils in a similar manner, and discriminated three regions. Di-2 EHPA adsorption, therefore, takes place through ligand exchange around the surface Al³⁺ and Fe³⁺ cations. Siffert and Trescol (1981) detected the formation of monodentate surface complexes, which probably also govern the process in a two-phase medium. The bidentate complexes, reported by Kafkafi *et al.* (1967) and Parfitt (1978) for inorganic phosphate anions seemingly cannot be formed with di-2 EHPA. The formation of surface complexes is distinctly more difficult in a water-decane system than in pure decane, due to the competition of water molecules for adsorption sites.

Reducing di-2 EHPA uptake

To avoid chemisorption of di-2 EHPA (formation of surface complexes), the reagents used should be capable of masking adsorption sites or displacing retained di-2 EHPA. Inorganic anions which can be specifically adsorbed on the surface cations of the octahedral sheet of clay were employed including: fluoride, readily adsorbed because its dimensions are approximately those of the hydroxyl anion (Dickman and Bray, 1941); dihydrogen-phosphate, an inorganic equivalent of the alkylphosphate anion specifically retained by aluminum cations (Wey, 1953; Parfitt, 1978); and phosphoric poly-anions, notable because of their marked and often irreversible adsorption (Van Olphen, 1977). Di-2 EHPA uptake can be avoided or reduced by resorting to: (1) pretreatment of H⁺-clays (adsorption sites are masked by fixation of inorganic anions before acid treatment); (2) "in situ" treatment (the sites of di-2 EHPA adsorp-

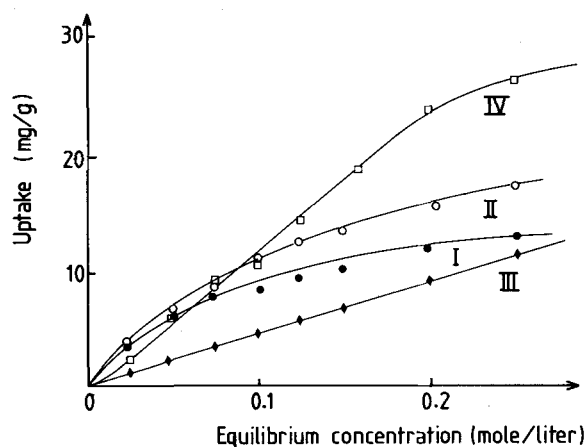


Figure 2. Adsorption isotherms of di-2 EHPA onto (I) H_2PO_4^- -kaolinite; (II) F^- -kaolinite; (III) H_2PO_4^- -montmorillonite; (IV) F^- -montmorillonite.

tion are masked by inorganic anions during paste preparation); or (3) aftertreatment (di-2 EHPA chemisorbed on clays is displaced by using a suitable anion).

Pretreatment

Before preparation of the pulp, the clays were pretreated with a large excess of inorganic anions to saturate all adsorption positions. Excess reagent was removed by repeatedly washing with distilled water. Chemisorbed anions must stand acid conditions ($\text{pH} = 1.5$) in a heated state (60°C) and not be displaced by di-2 EHPA.

Ten grams of clay were stirred three times for 24 hr with 1 liter of 0.1 M KF or dihydrogen phosphate solution. In the latter solution, maximum adsorption was achieved at $\text{pH} = 4.5$. The solids were washed three times for 3 hr with distilled water and dried at 40°C . Four modified clays were thus prepared: (1) F^- -kaolinite; (2) H_2PO_4^- -kaolinite; (3) F^- -montmorillonite and (4) H_2PO_4^- -montmorillonite.

Di-2 EHPA was determined radiochemically after preparation of the corresponding pulp by acid treatment. The isotherms are shown in Figure 2. Di-2 EHPA uptake on fluorinated clays (Curves II and IV) is higher than those reported by Siffert and Trescol (1981) for untreated clays. It follows, therefore, that new adsorption sites were created as silica sheets of the clay were attacked by the HF formed during the acid attack. This effect was amplified by desorption of fluoride anions, because adsorption of organic phosphate cannot take place on F^- -kaolinite or F^- -montmorillonite (Wey, 1953). The number of fluoride anions desorbed and, therefore, of adsorption sites created, is dependent on di-2 EHPA concentration. For the H_2PO_4^- -clay, adsorption increased linearly with equilibrium molarity for H_2PO_4^- -montmorillonite (Curve III) and reached a limit for H_2PO_4^- -kaolinite (Curve I). The equilibrium

Table 1. Polyphosphate concentrations necessary to reduce di-2 EHPA uptake.

Polyphosphate	Reduction to 2% of initial uptake onto H^+ -kaolinite (meq P/liter)	Reduction to 15% of initial uptake onto H^+ -montmorillonite (meq P/liter)
Pyrophosphate	100	100
Tripolyphosphate	120	150
Metaphosphate	300	300

between inorganic and organic phosphate anions seems to govern the mechanism.

"In situ" treatment

The "in situ" treatment consisted in adding anions to mask the adsorption sites during the acid preparation of the pulp. Fluoride anions cannot be used under these conditions, because clay minerals are attacked by HF. H_2PO_4^- is also precluded, because di-2 EHPA adsorption increases with H_2PO_4^- -kaolinite. Adsorption of phosphoric polyanions, however, gives rise to several bonds, thus rendering displacement more difficult (Van Olphen, 1977). Lyons (1964) reported that kaolinite takes up tripolyphosphate ($\text{Na}_3\text{P}_3\text{O}_{10}$) at the rate of one molecule per three sites of adsorption. A large excess of reagent is necessary, as half the tripolyphosphate decomposes within 2 hr of contact (Van Wazer, 1958). Experiments were made with sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) and metaphosphate (Graham's salt). Although long considered as a hexametaphosphate (NaPO_3)₆, metaphosphate is in fact a chain polymer (NaPO_3)_n with undefined molecular weight (Souchay, 1963), yielding cyclic or chain-like hydrolysis products (e.g., trimetaphosphate) in acid medium.

Polyphosphates in concentrations ranging from 0.001 to 0.1 mole/liter, were reacted with clay suspended in sulfuric acid, and the di-2 EHPA uptake was measured. Figures 3 and 4 show variation of di-2 EHPA uptake on H^+ -kaolinite and H^+ -montmorillonite in terms of polyanion concentration in the sulfuric acid solutions. Adsorption strongly decreases as polyanion concentration increases (Florescig *et al.*, 1979). The limiting value is zero for kaolinite (Curves I and III) and approximately 15% of the initial uptake with montmorillonite (Curves II and IV). Polyphosphate uptake increased with its concentration in the sulfuric acid solution, thus reducing the number of sites accessible to di-2 EHPA and, therefore, its adsorption. A value of 0.05 mole/liter of pyro- or tripolyphosphate is sufficient to reduce the uptake to 0.1 mg/g on kaolinite and to 1–2 mg/g on montmorillonite. For comparison, the polyanion concentrations were expressed in meq P/liter, on the assumption that each phosphoric link masks one site of adsorption (Table 1). Lower efficiency of metaphosphate is probably due to interference of hydrolysis products (Van Wazer, 1958).

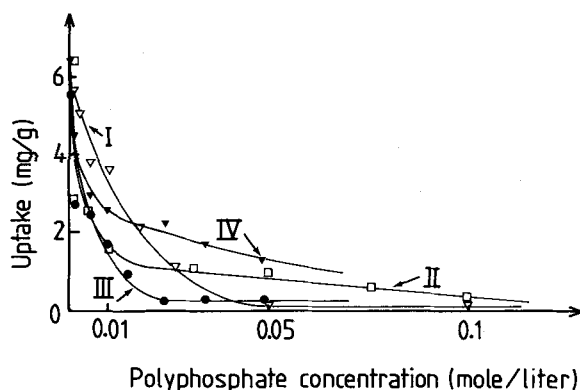


Figure 3. Uptake of di-2 EHPA in the presence of pyrophosphate onto: (I) H⁺-kaolinite; (II) H⁺-montmorillonite; and of tripolyphosphate onto (III) H⁺-kaolinite; (IV) H⁺-montmorillonite.

H₂PO₄⁻ anions are substantially less efficient than phosphoric polyanions (Figure 5). The curve yields a limiting value of 3.5 mg/g, i.e., 55% of the initial di-2 EHPA uptake, which confirms the existence of an equilibrium between inorganic and organic phosphate ions.

Aftertreatment

The di-2 EHPA-treated pulp was subjected to a desorption treatment. Alkylphosphate anions chemisorbed on the surface of the clays were displaced by a suitable anion. Hydroxyl and fluoride anions displace inorganic phosphate (Dickman and Bray, 1941) that is fixed on kaolinite at pH = 4 by the surface aluminum cations (Wey, 1953; Kafkafi *et al.*, 1967; Parfitt, 1978).

The clays were washed for 24 hr at ambient temperature with excess 0.1 M KOH, KF, or dihydrogen phosphate solution. No destruction or attack of the structure was observed. Hydroxyl anions normally desorb alkylphosphate at pH > 8, and 80% removal was achieved at pH = 11.2. Aftertreatments of montmorillonite with OH⁻ (at pH = 12.1) and F⁻ are identical (Figure 6,

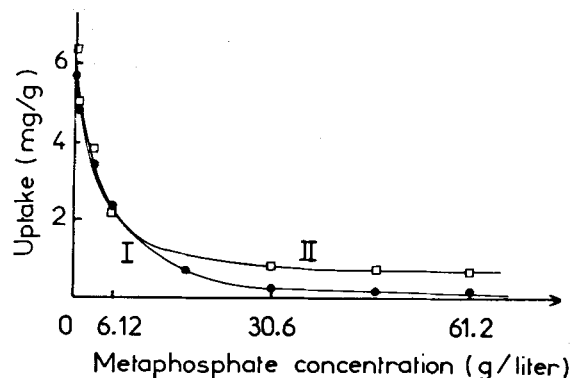


Figure 4. Uptake of di-2 EHPA in the presence of metaphosphate onto (I) H⁺-kaolinite; (II) H⁺-montmorillonite.

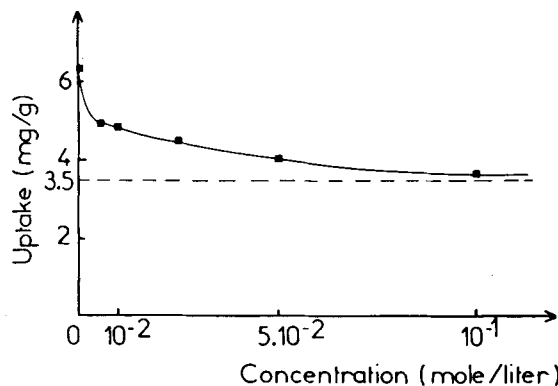


Figure 5. Uptake of di-2 EHPA onto H⁺-montmorillonite in the presence of dihydrogenphosphate.

Curves I and II) and allow 80% removal of the reagent. Curve III, obtained with H₂PO₄⁻, reveals the existence of an equilibrium between inorganic and organic anions and corresponds to 55% occupation of adsorption sites. By using fluorides, 90% removal of di-2 EHPA from kaolinite was achieved, but only 45% by using dihydrogen phosphate. These results also are indicative of an equilibrium between inorganic and organic phosphate anions, both for kaolinite and montmorillonite.

GENERAL CONCLUSIONS

The adsorption of di-2 EHPA on H⁺-clays is lower in a water-decane system than in decane alone. Accessibility of adsorption sites for organic acid molecules is more difficult in the presence of water and under acid conditions. Adsorption on H⁺-montmorillonite is less in a two-phase acid medium because only iron and aluminum cations retain their reactivity. The "stepped" shape of the adsorption isotherm suggests adsorption on different chemical sites. The presence of water fa-

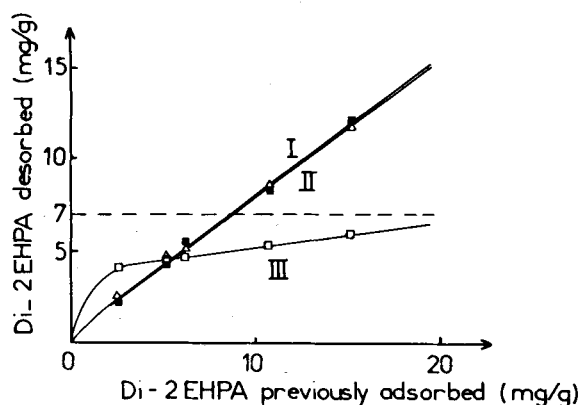


Figure 6. Desorption of di-2 EHPA from H⁺-montmorillonite after (I) washing with hydroxyl anions; (II) washing with fluoride anions; (III) washing with dihydrogenphosphate anions.

vors the creation of exchangeable groups on the surface Al^{3+} and Fe^{3+} cations. These groups of the $Al-(OH)_2^+$, $Al-OH$, or $Fe-OH$ type, exchange in a different way with the alkylphosphoric anions.

Reducing di-2 EHPA adsorption on H^+ -kaolinite and H^+ -montmorillonite is feasible by means of either an "in situ" or aftertreatment, whereas the use of fluorinated or phosphated H^+ -clays (pretreatment) increases di-2 EHPA uptake. Inorganic fluoride and phosphate anions attack the clay under the acid conditions of pulp preparation, thus creating new sites of adsorption. The "in situ" treatment leads to irreversible adsorption of phosphoric polyanion and reduces di-2 EHPA uptake by 95% and 85% for kaolinite and montmorillonite, respectively. Aftertreatment allows partial desorption of chemisorbed alkylphosphate. Although hydroxyl and fluoride anions allow significant recovery (80–90%), $H_2PO_4^-$ is substantially less efficient (20 to 35%) due to the existence of an equilibrium between organic and inorganic phosphate ions at the surface of clay.

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Резюме—Двухэтило2-гексилфосфорная кислота (di-2EHPA), растворенная в декане, хемисорбировалась на каолините и монтмориллоните, дисперсированных в кислотно-водном растворе. Результатом адсорбции является образование комплексов с поверхностными катионами глин. Изотермы адсорбции типа Лангмюра показывают предельную величину адсорбции на H^+ -каолините равную 12,2 мг/г, сравнимую с величиной, измеренной при отсутствии воды. В случае H^+ -монтмориллонита предельная величина в присутствии кислоты есть немного меньшая (20,6 мг/г по сравнению с 28,8 мг/г). Di-2EHPA не реагирует с катионами магния, доступными на поверхности. Кривая изотермы есть ступеньчатая, что возможно вызвано присутствием центров адсорбции с определенно различными энергиями. Центры адсорбции di-2EHPA могут быть маскированы действием анионов полифосфата на обе глины. Потому di-2EHPA подбор в кислотной среде является небольшим в присутствии пиро- и триполифосфатов. Адсорбированный di-2EHPA может быть получен обратно путем воздействия анионов флуорида, гидроксила и двухводородофосфата на глины. Присутствие анионов двухводородофосфата приводит к состоянию равновесия между органическими и неорганическими адсорбированными анионами фосфата. [E.C.]

Resümee—In Decan gelöste Bi-äthyl-2-hexylphosphorsäure (Di-2EHPA) wird an Kaolinit und Montmorillonit, die in einer sauren wässrigen Lösung dispergiert sind, chemisorbiert. Die Adsorption führt zur Bildung von Komplexen mit den Oberflächenkationen der Tonminerale. Die Adsorptionsisotherme sind vom Langmuir-Typ und zeigen bei H^+ -Kaolinit einen Grenzadsorptionswert von 12,2 mg/g, der mit dem Wert vergleichbar ist, der in der Abwesenheit von Wasser Gemessen wurde. Für H^+ -Montmorillonit ist dagegen der Grenzwert bei Anwesenheit der Säure etwas kleiner (20,6 mg/g vs. 23,8 mg/g). Di-2EHPA reagiert nicht mit den Magnesiumkationen, die an der Oberfläche vorhanden sind. Die Isotherme hat Stufenform und weist auf Adsorptionsstellen mit deutlich unterschiedlichen Energien hin. Die Stellen für die Di-2EHPA-Adsorption können maskiert werden, indem die beiden Tonminerale mit Polyphosphatanionen behandelt werden. Das heißt die Aufnahme von Di-2EHPA ist bei Vorhandensein von Pyro- und Tripolyphosphatanionen in sauren Medien sehr gering. Die adsorbierte Di-2EHPA kann durch eine Behandlung der Tonminerale mit Fluorid-, Hydroxyl-, und Dihydrogenphosphatanionen wiedergewonnen werden. Die Dihydrogenphosphatanionen führen jedoch zu einem Gleichgewichtszustand zwischen den adsorbierten organischen und anorganischen Phosphatanionen. [U.W.]

Résumé—L'acide bis-éthyl 2-hexylphosphorique (di-2 EHPA) en solution dans le décane est chimisorbé sur la kaolinite et la montmorillonite, dispersées dans une solution aqueuse acide. L'adsorption s'effectue sur les cations superficiels de la structure avec formation de complexes de surface. Les isothermes sont du type Langmuir et mettent en évidence sur la kaolinite- H^+ une valeur limite d'adsorption de 12,2 mg/g, comparable à celle mesurée en absence d'eau. Avec la montmorillonite- H^+ , la valeur limite d'adsorption en présence de la phase aqueuse acide est, par contre, plus faible (20,6 mg/g au lieu de 23,8 mg/g). Les cations magnésium présents en surface de la montmorillonite ne réagissent plus avec le di-2 EHPA. L'isotherme présente des "marches" et traduit la présence de sites d'adsorption d'énergie nettement différenciée. Les sites d'adsorption du di-2 EHPA peuvent être masqués par traitement des deux phyllites avec des anions polyphosphate. Ainsi, avec les anions pyro et tripolyphosphate, la fixation du di-2 EHPA en milieu acide est très faible. Le di-2 EHPA fixé sur les argiles peut aussi être récupéré en traitant les argiles avec des anions fluorure, hydroxyle, et dihydrogénophosphate. Avec l'anion dihydrogénophosphate, on obtient toutefois un état d'équilibre entre les anions phosphate organiques et minéraux adsorbés.