CONTRIBUTION TO THE ADSORPTION MECHANISM OF ACETAMIDE AND POLYACRYLAMIDE ON TO CLAYS

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Abstract—While studying the retention of additives used in tertiary recovery of petroleum (waterflooding) on minerals present in a rock reservoir, an investigation has been undertaken into the adsorption mechanism of polyacrylamides on to clays. The adsorption of amides and polyacrylamides takes place exclusively on the external surfaces of the clay particles. The organic molecules are protonated on the surface and adsorbed by ionic forces. There is a linear relationship between the adsorption ratio and the polarizing power of the exchangeable cations of the clay mineral. The adsorption isotherms and the thermal analyses reveal the existence of two adsorption mechanisms: (i) a strong, irreversible adsorption, which corresponds to the formation of a monolayer of chemisorbed molecules, (ii) a more important adsorption of molecules retained by hydrogen bonding, which can be eliminated by heating at low temperature. The retention ratio in the irreversible process, which is practically identical both for acetamide and polyacrylamide, is low (3 mg/g). It depends on the external cation exchange capacity (CEC) of the mineral and increases with the surface area. The polyacrylamide adsorption depends on the physico-chemical characteristics of the macromolecule, more particularly on the $CONH_2/COO^-$ ratio, which determines the extent of the carbon chain, and the molecular weight. The accessibility of the organic macromolecule to the clay particle is controlled by the preceding factors. The quantity of polyacrylamide irreversibly adsorbed by clay minerals is important in the context of the use of the polymer on a petroleum field. It may be reduced to a minimum by working at low concentrations with a weakly hydrolyzed polyacrylamide solution.

INTRODUCTION

This work aims at a better understanding of the interaction and uptake mechanism of partially hydrolyzed polyacrylamides, used in 'tertiary' recovery of petroleum, by the mineral substrate. Indeed, a stimulation or thorough recovery is carried out in order to improve the yield of the oil reservoir. It consists of the injection of a fluid, water (waterflooding), with a view to replacing the remaining petroleum.

However, owing to a difference of viscosity between water and petroleum, various additives are incorporated into the 'piston' fluid in order to modify its mobility. High molecular weight polymers, particularly polyacrylamides, are used to this end. These are acrylamide–acrylic acid copolymers with the following structure:

$$60 \leqslant x \leqslant 95\%$$
$$5 \leqslant y \leqslant 35\%$$
$$z < 5\%$$
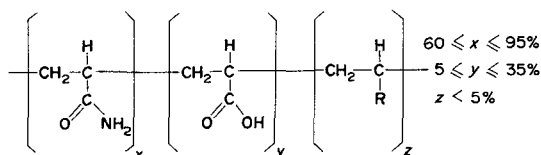
When applied to petroleum treatment, the degree of hydrolysis y generally ranges from 5 to 30%. These polymers, which have been previously used for flocculation (Michaels and Morelos, 1955; Ruehrwein and Ward, 1952), act simultaneously on water viscosity and rock porosity in diluted aqueous solution.

The investigations carried out on scale models of deposits showed a rock porosity decrease and a marked loss of polymer. The factors involved in the loss or uptake of polyacrylamides by the rock medium are very numerous if the variation of mineralogical composition in the deposit, structural intricacy and behavior in liquid medium of the organic macromolecule are taken into account at the same time. Yet, irrespective of the surmise which may be considered concerning the retention phenomenon, it can be reasonably assumed that the surface area of the mineral must be at least quantitatively involved.

Among the minerals commonly encountered in crude oil deposits which display high specific areas, the phyllosilicates and particularly swelling clays of the smectite group are to be mentioned. We restricted our investigation, for the time being, to the interaction of polyacrylamides with clays.

Burcik (1965, 1967, 1968) assumes that the decrease of rock porosity and the loss of polymer originate from the clogging of storing rock micropores by microgels existing in the polyacrylamide solutions. A number of authors, Mungan (1966, 1969) and Smith (1968, 1970) among others, assume that the porosity decrease originates essentially from polymer adsorp-

tion by the rock, thus leading to a loss of waterflooding efficiency as a function of the distance covered by the solution. Yet, no surmise has been put forward concerning a precise adsorption mechanism.

Other works regarding the use of polyacrylamides in tertiary recovery of petroleum have been reported (Pye, 1964; Sandford, 1964; Patton, 1969; Rakhimkulov and Babalyan, 1969; Fulford, 1969), but are primarily concerned with petroleum technology. None of them specifies the adsorption and interaction mechanism of these compounds with minerals present in the rock reservoir.

A more theoretical investigation of the problem was carried out by Schamp and Huylebroeck (1973), who studied soil conditioning. These authors studied the flocculating effect of polyacrylamides on clay suspensions. They determined the adsorption isotherms of montmorillonite by polymers with molecular weights ranging from 10^5 to 10^6. From their kinetic adsorption curves, Schamp and Huylebroeck concluded that two adsorption species exist: a 'surface' one and another 'in the pores'. Ruehrwein and Ward (1952) are of the opinion that the adsorption of anionic polymers occurs through ionic exchange, which involves the replacement of hydroxyls by carboxylate ions. Michaels and Morelos (1955) suggest that adsorption is mainly conditioned by hydrogen bonding between the solid on the one hand, and the nonionized hydroxylic, amidic and carboxylate functions of the macromolecule on the other hand. A third bonding possibility would originate from the interaction between polyvalent cations (Ca^{2+}), acting as crosslinking agents between the solid surface and the polymer. The adsorption of an anionic polyelectrolyte is not necessarily attended by flocculation. When it occurs, it involves a bridge linkage of polymer molecules between solid particles. Bontoux et al. (1972) showed that (i) the extension of the chain promotes the formation of interparticle linkages, (ii) the pH increases the negative charges of polyelectrolyte and bentonite and makes the electrostatic repulsions stronger.

The bibliographical survey prompts the following conclusions: (a) The adsorption and interaction mechanism of polyacrylamides with clays is little understood and actively discussed. (b) The data giving the quantities of adsorbed polymer were all measured by viscometric or turbidimetric titration of residual aqueous solutions, disregarding both a selective adsorption of a polymer fraction having a given molecular weight and a possible polymer degradation during the experiments. (c) The interaction mechanisms based upon previous measurements are incomplete. (d) The adsorption phenomenon was never proved to be irreversible.

In view of the complexity of the phenomena, we deemed it proper to undertake a restricted investigation, as carefully as possible, regarding the determination of the adsorbed amounts. That is the reason why we determined it through the micro-Kjeldahl method,

which yields the total amount of nitrogen taken up. In order to investigate the mechanism of polymer uptake on to clay, we used infrared spectroscopy. However, owing to the high molecular weight of the polymer and the intricacy of its molecule, in addition to its flocculating properties which make difficult the preparation of samples for investigation, the interpretation of the spectra proved to be too difficult. We approach therefore the problem by investigating the adsorption of a small molecule on to clay: acetamide.

The present work is divided into two main parts. The first one deals with the adsorption of acetamide on to various clays, taking into account all parameters involved. The adsorption data of various polyacrylamides are shown in the second part, with emphasis on the significance of two parameters, the degree of acrylic acid–acrylamide copolymerization (also called degree of hydrolysis) and the molecular weight of the polymer.

INVESTIGATION OF THE ACETAMIDE–CLAY ADSORPTION MECHANISM

For reasons already described, the acetamide molecule (CH_3CONH_2) was taken as a model for the investigation of the amide–clay interaction, rather than formamide ($HCONH_2$) which, unlike the other amides, displays a number of unique physical and chemical properties. The acetamide molecule makes it possible to d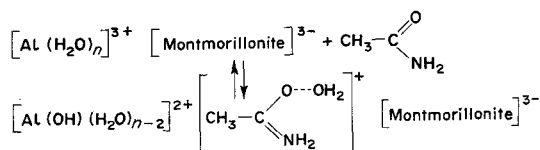etermine the type of bonding which may appear between a $-C\overset{O}{\underset{NH_2}{\diagdown}}$ group and the clay particle. In fact, according to Michaels (1954), the carbonylic groups, as well as the carboxylic anions carried by the organic macromolecule, should not be involved in the retention phenomenon. This author believes that such structural patterns contribute merely to the lengthening of the carbon chain in the polyacrylamide molecule, through a charge-repulsion effect. This statement is supported by the work of Wey and Sieskind (1959) about the adsorption of carboxylic acids by montmorillonite. Mortland et al. (1966, 1969, 1971) published several papers concerning the interaction of montmorillonite with primary, secondary and tertiary amides. Amides, which are derivatives of carboxylic acids, may react by involving both their carbonylic electrons and those located on the nitrogen atom. Hence, the amide molecule exhibits a resonance structure of the following type:

$$R-C\overset{O}{\underset{NH_2}{\diagdown}} \longleftrightarrow R-C\overset{O^-}{\underset{\underset{+}{NH_2}}{\diagdown}}$$
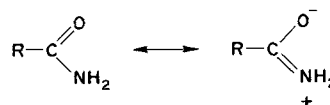
This symbolism, which was described by Pauling (1960) and Fieser (1961), accounts both for the shortening of the C—N bond (in proportion to the corresponding amines) and the special stability of amides. Mortland (1971) describes four possible reaction
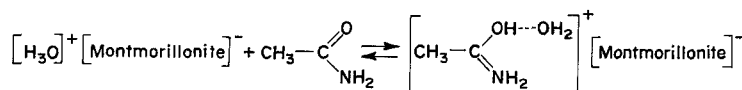
mechanisms which may be involved in the adsorption phenomenon of amide molecules on clays. These are ion exchange of protonated molecules, hemisalt formation, coordination complexes with exchangeable cations and hydrogen bonding.

Upon completion of an investigation of the montmorillonite–amide complexes by infrared spectroscopy, Tahoun and Mortland (1966a) concluded in favor of the following mechanism:

$$\left[AL(H_2O)_n\right]^{3+} \left[Montmorillonite\right]^{3-} + CH_3-C\overset{O}{\underset{NH_2}{\diagdown}}$$

$$\left[AL(OH)(H_2O)_{n-2}\right]^{2+} \left[CH_3-C\overset{O\cdots OH_2}{\underset{NH_2}{\diagdown}}\right]^{+} \left[Montmorillonite\right]^{3-}$$

This protonation would occur directly on the surface of the clay particles.

In a further study concerning montmorillonite saturated with metal cations, Tahoun and Mortland (1966) found evidence for the existence of a direct coordination bonding between the amidic oxygen atom and the exchangeable cation of the mineral. Yet, the introduction of amide into the clay interlayer spacing is implied by this second mechanism. Farmer and Ahlrichs (1969) assume a similar mechanism (direct amide complexing on the exchangeable metal cation of the phyllite, involving the oxygen atom) and give the order of stability of the montmorillonite complexes ($Na^+ < Ca^{2+} < Ni^{2+} < Al^{3+}$). Upon studying the adsorption of secondary amides on to a trimethylammonium exchanged montmorillonite, Doner and Mortland (1969) concluded in favor of the existence of hydrogen bonding between a hydrogen of the trimethylammonium and the oxygen of the carboxylic group. Recently, Tahoun (1971) suggested a water molecule bridging between the acetamide molecule and the 'acid' montmorillonite:

isms suggested. Moreover, a fundamental ambiguity lies in the location of the adsorption sites, some studies having proved the presence of interlayer compounds, obtained, and this must be stressed, by using very high amide concentrations. The present investigation is aimed at establishing the mechanism of low concentration acetamide interaction with clays in aqueous medium. In practice it should be remembered that only low concentration polyacrylamide solutions are used in tertiary recovery of petroleum.

The clay used in this work is a montmorillonite, named 'K.L.' and supplied by CECA Ltd (France). It is of Greek origin. In order to have materials available with clearly defined properties, the clay was treated first with 0.5 N HCl to eliminate iron-containing impurities, then purified in a neutral medium by repeated lixiviation with a normal sodium chloride solution. Finally, the sodium clay was washed until the residual salt was eliminated. Analytically pure acetamide was purchased from Prolabo Ltd (Reference: 20055).

In order to investigate acetamide adsorption at a constant temperature, known amounts of montmorillonite were introduced into acetamide solutions of variable concentrations (0.25–2.5 g/l). The clay suspensions were next stirred for 24 hr, without pH adjustment (pH $\simeq$ 7). After centrifugation, the montmorillonite was washed with distilled water and dried. The amount of acetamide irreversibly fixed was obtained by micro-Kjeldahl nitrogen determination.

The amount of acetamide fixed on the montmorillonite depends both on the initial acetamide concentration in the solution and on the 'relative' acetamide concentration in proportion to the weight of montmorillonite which is involved. The shape of the adsorption isotherm therefore varies slightly with the procedure. Figure 1 shows two isotherms obtained by bringing into contact 0.5 and 1 g of montmoril-

$$\left[H_3O\right]^{+}\left[Montmorillonite\right]^{-} + CH_3-C\overset{O}{\underset{NH_2}{\diagdown}} \rightleftarrows \left[CH_3-C\overset{OH\cdots OH_2}{\underset{NH_2}{\diagdown}}\right]^{+} \left[Montmorillonite\right]^{-}$$

In the case of kaolinite, which has a much lower CEC than montmorillonite, Ledoux and White (1966) assumed an adsorption of primary amide by physisorption and the formation of hydrogen bonds between the oxygen of the carbonylic groups and the surface hydroxyls of the mineral, as well as between the hydrogen atoms of the NH_2 groups and the oxygen atoms of the siloxanic surfaces.

Another attempt to introduce amides in clay was carried out by Olejnik et al. (1971), who achieved acetamide intercalation by heat-treatment at the melting temperature at 105°C. No intercalation is observed even after 4 days, but 63% after 203 days.

In general, the studies reported in the literature are mostly concerned with qualitative investigations, which account for the variety of interaction mechan-

lonite respectively in 20 ml of aqueous acetamide solution with an analytical concentration varying between 0.25 and 2.5 g/l. Both isotherms tend towards the same limit, but their aspect is slightly different. For experimental convenience and in order to obtain comparable curves, we chose to use always 1 g of clay dispersed in 20 ml of aqueous acetamide solution, except where otherwise stated. However, it should be remembered that the adsorption limit (plateau of the curves) remains unchanged, whatever the procedure. The aspect of the curves follows in each case Langmuir's adsorption equation.

To make sure that the adsorption is irreversible, we studied the amount of acetamide adsorbed on Na^+ montmorillonite as a function of the number of washings. Figure 2 shows the results obtained. It
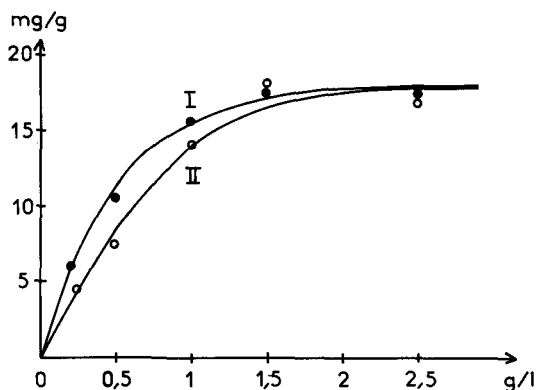
Figure 1. Influence of relative concentrations on the shape of adsorption curves: (I) 0.5 g montmorillonite, (II) 1 g montmorillonite.

Figure 3. Adsorption isotherms for acetamide on Na-montmorillonite at 20°C: influence of drying temperature.

is apparent that the weakly retained acetamide is wholly removed by the second washing. The amount of bound acetamide remains therefore constant whatever the volume of water involved. The acetamide fixation is thus confirmed, precluding an exchange phenomenon between the molecules of water and acetamide on the surface of the mineral. In the course of the subsequent experiments, the adsorbent always was washed three times successively.

In the liquid phase, the fixation appears irreversible and constant for a given temperature. Upon drying, several orders of magnitude of acetamide fixation on to the montmorillonite are disclosed, depending on the drying method and consequently the percentage of residual water in the mineral. By way of example, the amount of bound organic compound, determined after vacuum drying at room temperature, is considerably higher than that obtained with oven drying (60°C). Figure 3 shows the isotherms obtained according to both drying procedures. It is apparent that, depending on the method, the limiting values of the adsorption exhibit significant variations.
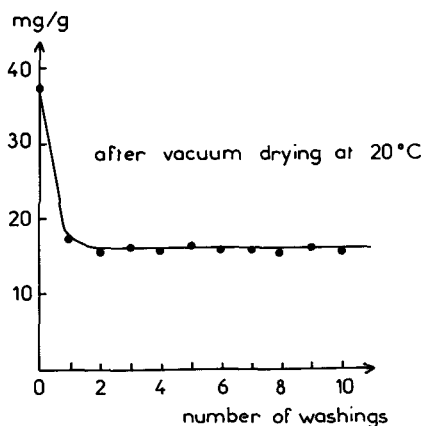
The adsorption limit at 3 mg of acetamide per gram

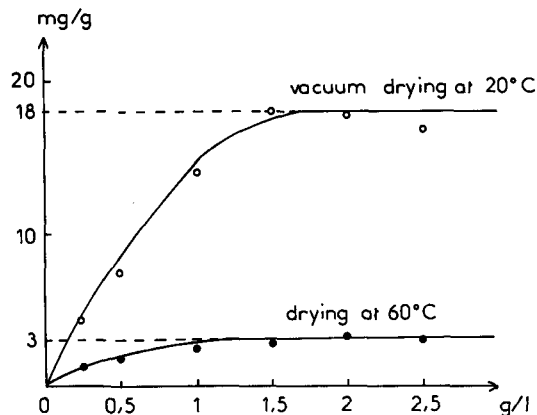Figure 2. Relationship between the amount of acetamide adsorbed on to Na-montmorillonite and the number of washings.

of montmorillonite after drying at 60°C may be considered as a 'true', intense fixation, corresponding to a chemisorption. On the other hand, the limit at 18 mg/g, observed with vacuum drying over drierite, and which, consequently, is a partial one, corresponds rather to an unstable adsorption equilibrium. In fact, when the drying temperature of these complexes is brought up to 60°C, the values of the 'true' fixation are found again. At the same time, the proportion of residual humidity in the clay decreases from 14 to 10%. So when the clay–acetamide complex is dried at high temperature, part of the water escapes taking with it some acetamide as this would be the case for a classical steam distillation. It would appear that two types of adsorption occur concurrently, a reversible physisorptive and an intense, irreversible chemisorption. The contribution of the first fixation type appears to be dependent on the proportion of residual water retained by the montmorillonite.

Therefore the amount of bound acetamide depends on the association mode of the organic molecules and the hydration state of the clay. In order to verify this hypothesis, a run of adsorption experiments was performed at 60°C, under the same conditions as those at the room temperature experiments. The drying was carried out under vacuum, over drierite, at room temperature. The results are plotted in Figure 4. Although a drying treatment was performed at room temperature, the adsorption maximum is found to be situated in the vicinity of 3.5 mg/g, a value very close to that of the 'intense' adsorption or chemisorption. This experiment confirms the hypothesis of a double fixation, the most labile one decreasing as the temperature increases.

The adsorption isotherms depend also on the nature of the exchangeable cation. In Figure 5, we plotted the isotherms for a montmorillonite saturated with various monovalent cations, i.e. carrying equal charges but having different ionic radii. The Li^+ and Cs^+ montmorillonites have been prepared from sodium montmorillonite through ion exchange, by bringing the sodic mineral into contact with a molar
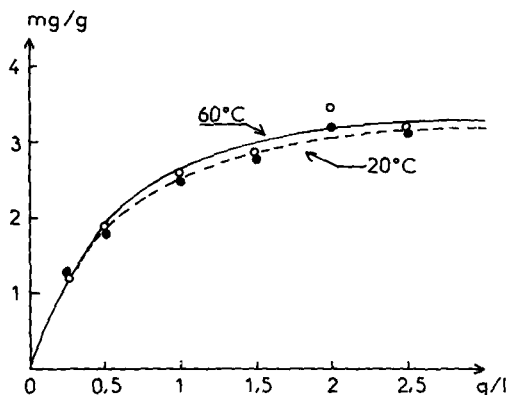
Figure 4. Adsorption isotherms for acetamide on Na montmorillonite: influence of adsorption temperature.
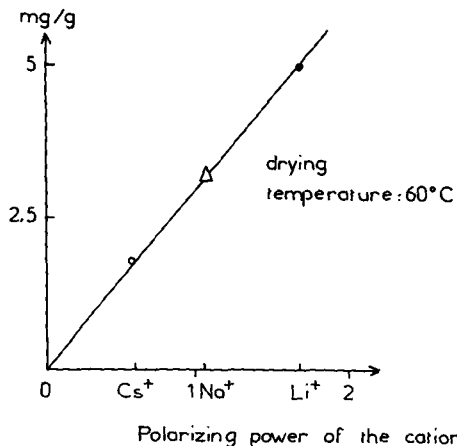

Figure 6. Relationship between the amount of adsorbed acetamide and the polarizing power of the exchangeable cation.

solution of the corresponding alkaline chloride and then washing until the chloride ions are completely eliminated. The adsorption maxima are found to be in the following order: $Li^+ > Na^+ > Cs^+$, which reflects the order of decreasing polarizing power of the cations. A linear correlation is found between the adsorption maxima and the polarizing powers, the phenomenon being particularly clear in the case of 'intense' adsorption (Figure 6). The phenomenon of acetamide adsorption depends therefore on the nature of the interlayer cation.

As kaolinite is a very common clay mineral, we performed a similar study with this silicate. Kaolinite does not exhibit any interlayer CEC. It cannot swell, so acetamide can only be fixed on the external surface, if ever adsorption occurs. The kaolinite used for this study exhibits an exchange capacity of 3 mequiv./100 g of clay, calcined at 1000°C. A first experiment, performed with this mineral, according to the aforementioned procedure, provided evidence for weak adsorption, within experimental error. Therefore, the procedure has been modified accord-

ingly: 2 g of mineral were dispersed in 200 ml of acetamide solutions with concentrations ranging from 0.125 to 1.25 g/l. The resulting adsorption isotherm is represented in Figure 7. The maximum adsorption is situated in the vicinity of 1.3 mg/g. This value corresponds to 2.2 mequiv./100 g of kaolinite calcined at 1000°C, and approximates very closely the exchange capacity of the mineral.

The investigation of acetamide adsorption on clays provides evidence for two separate adsorptive limits on montmorillonite: the smaller one corresponds to a marked adsorption (chemisorption), the highest one to a labile adsorption (physisorption). These two types of adsorption are conditioned by the polarizing power of the interlayer cation, and exhibit an irreversible character in solvent medium. The labile adsorption becomes very weak as the adsorption temperature increases, the stronger one being not affected. Moreover, the stronger adsorption displays similar orders of magnitude, both in the cases of montmorillonite and of kaolinite. Bearing in mind that the uptake on kaolinte can only be external, the hypothesis of acetamide uptake on clays through the external surfaces of the crystallite must be considered. Infrared spectroscopy and X-ray diffractometry have been done to clarify the interaction mechanism.
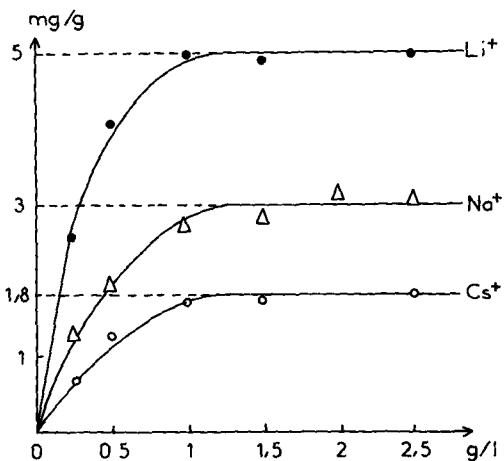

Figure 5. Adsorption isotherms for acetamide on Na-montmorillonite at 20°C: influence of the exchangeable cation; drying temperature 60°C.
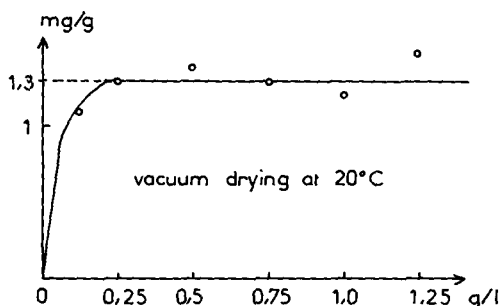

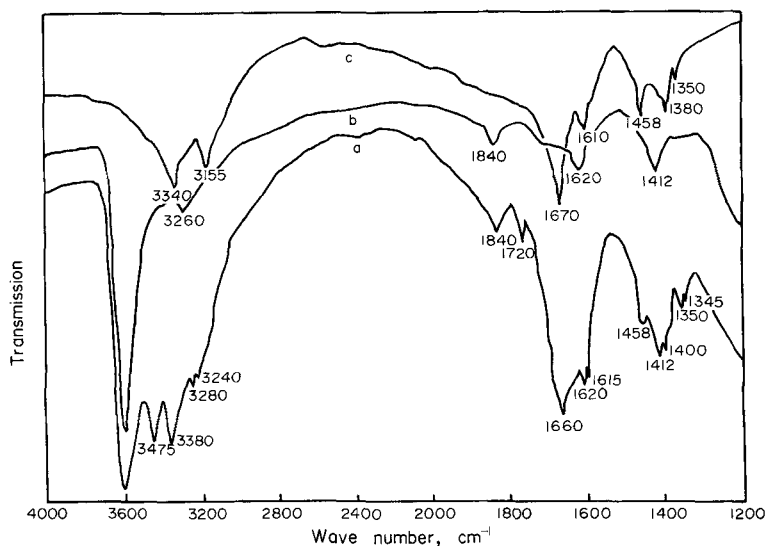Figure 7. Adsorption isotherm for acetamide on Na-kaolinite.

Figure 8. Infrared spectra of (a) acetamide–Na montmorillonite complex, (b) Na-montmorillonite, (c) acetamide.

(a) *Infrared spectrometry of acetamide–montmorillonite complexes*

Self-supporting films of acetamide–clay complexes were prepared according to an already known procedure (Farmer, 1969; Fripiat, 1966; Mortland and Tahoun, 1966). These films having 4 mg/cm^2 were prepared by evaporating at room temperature aqueous suspensions of montmorillonite both with and without acetamide. Films with kaolinite could not be prepared and, accordingly, infrared spectrometry has not been applied to this mineral. The spectra were recorded on a Beckman infrared spectrophotometer I.R. 20, from 2.5 to 40 μm (4000–250 cm^{-1} period: 2, amplification: 5, slit: 3). Reference spectra were obtained by using the pellet procedure with potassium bromide at the relative concentration of 2%. The spectra of Na$^+$ montmorillonite, pure acetamide and acetamide–montmorillonite complex dried at room temperature are shown in Figure 8. Table 1 displays the principal infrared bands of the three samples, their assignment and eventual development. Two differences are found concerning the vibration bands of acetamide adsorbed on montmorillonite; a mean intensity band at 1720 cm^{-1}, attributable to a C=N stretching vibration, and a weaker one at 1345 cm^{-1}, which may be assigned to an OH deformation vibration. According to Albert and Badger (1958), Spinner (1960), Kutzelnigg and Mecke (1962), these bands are found in the spectrum of acetamide chloride. The strongest of them is present in the acetamide–montmorillonite complex spectrum. It follows that a small fraction of

Table 1. Infrared frequencies (cm^{-1}) of (i) Na$^+$ montmorillonite (ii) acetamide and (iii) Na$^+$ montmorillonite–acetamide complex
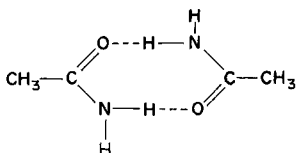
Na$^+$ montmorillonite	Acetamide	Montm.–acetamide complex	Assignment	Shift Δv(cm^{-1})
3600	—	3600	Montm. v (OH)	
—	3340	3475	$v_{as.}$ (NH$_2$)	+135
		3380		
	3155	3280	$v_{as.}$ (NH$_2$)	+225
3260	—	3240	Montm.	
1840	—	1840	Montm.	
—	—	1720	v (C=N)	New band
—	1670	1660	v (C=O)	−10
1620	—	1620	(H$_2$O) mineral	
—	1610	1615	δ(N—H) amide II	+5
—	1458	1458	$\delta_{as.}$ (CH$_3$)	
1412	—	1412	Montm.	
—	1380	1400	v (C—N)	+20
—	1350	1350	$\delta_{s.}$ (CH$_3$)	
—	—	1345	δ (O—H)	New band

the acetamide would be adsorbed in the following protonated form:

$$CH_3-C\begin{array}{c} OH \\ \diagdown \\ NH_2 \\ + \end{array}$$
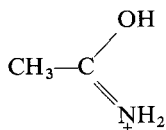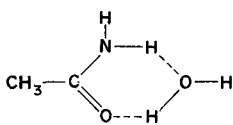
on the clay surface.

Concurrently with the appearance of the previously described bands, a slight shift of the bands at 1670 cm^{-1} ($\Delta\nu$ = 10 cm^{-1}), attributable to a C=O stretching vibration and at 1380 cm^{-1} ($\Delta\nu$ = +20 cm^{-1}), which can be assigned to a C—N stretching vibration, were recorded. In addition, the symmetric and asymmetric stretching bands of NH$_2$ at 3340 and 3155 cm^{-1} shift to 3475 and 3380 cm^{-1}. According to Bellamy (1958) these band shifts would result from the presence of acetamide hemisalts. Indeed, the intermolecular hydrogen bonds bring about a significant modification in the vibrations of the NH$_2$ group. The shifts of the C=O and C—N stretching vibrations may therefore be accounted for by an additional delocalization of the electron pair through several molecules. This part of the spectrum suggests that a significant fraction of the acetamide molecules fixed by the mineral are fastened together by bridge linkages, as follows.

$$\begin{array}{c} \quad\quad\quad\quad H \\ \quad O\text{---}H-N \\ CH_3-C \diagup\quad\quad\quad\diagdown C-CH_3 \\ \quad\quad N-H\text{---}O \\ \quad\quad\quad H \end{array}$$

Yet, another type of hydrogen bonding involving water bridges may also be considered, the band shifts being similar in this case.

$$\begin{array}{c} \quad\quad H \\ \quad\quad N\text{---}H \\ CH_3-C\quad\quad\quad\diagdown \\ \quad\quad\quad\quad O-H \\ \quad O\text{---}H \end{array}$$

Thus, investigation of infrared absorption spectra of room temperature-dried complexes shows the presence of two types of adsorbed acetamide molecules on clay surface, protonated and hydrogen bonded molecules.

We also investigated the dehydration of the acetamide–montmorillonite complexes at different temperatures. For this purpose, a special cell fitted with a furnace has been used. The samples were evacuated at room temperature under a pressure of 13.3 Pa and then heated at various temperatures (from 20 to 150°C) for half an hour. After each heating, the sample was allowed to cool down before the spectra could be recorded. A gradual decrease in the intensity of all bands relating to non-protonated acetamide and loosely surface-bound water can be observed as a function of the treatment temperature. The weakest

bands disappear after prolonged heating. At the same time, both bands specific of protonated acetamide molecules and montmorillonite remain unchanged. Further, it should be noted that the band at 1615 cm^{-1} (N—H deformation vibration) is slightly shifted to a lower frequency, while its intensity decreases. The band at 1660 cm^{-1} (C=O stretching vibration) displays a similar change. This phenomenon corresponds to a breaking of hydrogen bonds between the C=O and NH$_2$ groups of neighboring acetamide molecules, resulting in gradual elimination of acetamide molecules loosely bonded to the surface of the mineral. This phenomenon occurs mainly at low temperature ($<50°C$). On the other hand, the bands specific to the protonated form endure: so, the spectrum recorded under these conditions is much the same as in the case of a complex oven-dried at 60°C. Further information could be gathered by deuteration of acetamide–montmorillonite complexes. Upon evacuation in the special cell, the sample is allowed to stand under a saturating atmosphere of D$_2$O vapor. The operation is repeated, in order to gradually exchange the hydrogen atoms with deuterium atoms. Bands recorded before evacuation and after seven contacts are compared in Table 2: deuteration shifts some acetamide bands. A spectrum resembling that of CH$_3$COND$_2$ has been recorded (Garrigou-Lagrange, 1974). Moreover, the interactions originating from intermolecular bonding are little altered by the H $\rightleftharpoons$ D exchange. As the spectrum of N-deuterated acetamide chloride is not known, it may be inferred that the exchange also occurs on the molecule

$$CH_3-C\begin{array}{c} OD \\ \diagdown \\ ND_2 \\ + \end{array}$$
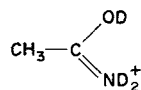
as a result of the disappearance of the δ(O—H) band at 1345 cm^{-1} and as a slight band shift occurs at 1720 cm^{-1} (C=N stretching vibration). Therefore deuteration affects both acetamide forms. Since, the oxygen and nitrogen bound hydrogen atoms are exchangeable, it may be inferred that neither the oxygen nor the nitrogen are involved in a 'covalent' bond with the mineral.

Table 3 gives the discrepancies which can be observed between the spectra of various monovalent cationic saturated montmorillonite in the regions 1800 and 1300 cm^{-3}. It should be noted that the spectra of Na$^+$ and Li$^+$ montmorillonite complexes are almost identical. On the other hand, the spectrum of acetamide–Cs$^+$ montmorillonite complex displays a weakening of the acetamide mean intensity bands (which was to be expected, as the adsorbed quantity in this case is lower by 60%) and two peculiarities: (i) appearance of a band at 1530 cm^{-1}, (ii) splitting of the band at 1400 cm^{-1} (1395 and 1375 cm^{-1}). It is difficult to interpret these changes. Possibly they may be explained by taking into account the hydration shell of the exchangeable cations. The Cs$^+$ cation, which is bulkier and therefore less hydrated,

Table 2. Infrared frequencies (cm^{-1}) of acetamide–montmorillonite complex (i) before and (ii) after deuteration

Before deuteration (cm^{-1})	After deuteration (7 contacts) (cm^{-1})	Assignments
3600	3600	Structural hydroxyls of montm.
3475		$\nu_{asy.}(NH_2)$
3380		$\nu_{sym.}(NH_2)$
3280	3280	}Structure of montmorillonite
3240	3240	
	2650	$\nu_{asy.}(ND_2)$
	2495	$\nu_{sym.}(ND_2)$
1840	1840	Structure of montmorillonite
1720		
	1710	$\nu(C=N)$
1660		
	1645	$\nu(C=O)$
1620		$\delta(H_2O)$ water molecules
1615		$\delta(N-H)$
1458		
	1440	$\delta_{asy.}(CH_3)$
1412	1412	Structure of montmorillonite
	1420	
1400		$\nu(C-N)$
	1360	$\delta_{sym.}(CH_3)$
1350		
1345	not observable ($<1200\ cm^{-1}$)	$\delta(O-H)$

would display a more direct bonding to the acetamide. A coordination bonding between acetamide molecule and exchangeable cation may be considered, as was suggested by Mortland and Tahoun (1966). The band at $1530\ cm^{-1}$ which is specific to a 'secondary' amide, seems to imply that the nitrogen atom of the organic molecule is involved in the coordination. Yet this bonding relates only to a small amount of the acetamide and the coordination-generated 'complex' appears as very 'unstable'. This band, as well as the band of non-protonated acetamide, disappears on a slight heating. It is therefore apparent that the nature of the exchangeable cation exerts no qualitative influence on the fixation of protonated acetamide. The investigation by infrared spectroscopy of the complexes previously obtained points to the existence of two types of acetamide molecules adsorbed on clay: (i) the first type, in low proportion, is made up of a protonated acetamide molecule (cationic form). The bonding to the mineral is ionic, approximating a chemisorption. (ii) the second type, accounting for the major part, is concerned with molecules fastened together by hydrogen bonding or water molecules retained on the surface of the mineral. This retention corresponds to a physical adsorption.

Now, the location of the adsorption sites of both molecule types is unknown. In order to gain information about the adsorption sites, interlamellar or superficial, we used X-ray powder diffraction.

(b) X-ray powder diffraction study of acetamide–montmorillonite complexes

A better insight into the reaction mechanism and the nature of the bonding between acetamide and montmorillonite implies the location of the adsorp-

Table 3. Infrared frequencies (cm^{-1}) of acetamide–montmorillonite complexes; influence of the nature of the exchangeable cation of the mineral

Na+-montmorillonite complex (cm^{-1})	Li+-montmorillonite complex (cm^{-1})	Cs+-montmorillonite complex (cm^{-1})
1720	1720	1720
1660	1660	1660
1620 (mean)	1620 (mean)	1620 (weak)
1615	1615	1615
—	—	1530
1458	1458	1458
1400	1400	1395
		1375
1350	1350	1350
1345	1345	1345

tion site on the phyllite crystal, as the stated molecules may be adsorbed on to the surface as well as in the interlayer space of mineral. We already mentioned that the adsorption on kaolinite occurring on the external surface is comparable to that of montmorillonite. Therefore, similar behavior may be assumed, yet a close examination of the montmorillonite interlayer spacing is required to ascertain this result.

The interlamellar spacing in a sodium montmorillonite depends on its water content. So in a relative humidity of 50%, the basal spacing of montmorillonite is 12.5 Å, which corresponds to a monolayer of water molecules (Brown, 1961). For X-ray analysis and in order to obtain oriented clay aggregates, suspensions of acetamide–Na$^+$ montmorillonite complexes were allowed to settle on glass slides at room temperature. The samples were then put into a desiccator with a relative humidity of 52% (saturated NaHSO$_4$ solution). The diffractograms were recorded by using a spectrometer ($2° < 2θ < 10°$), under the following conditions: divergence and diffraction slits of $(1/6)°$, receiving slit of $(1/10)°$, Cu K$_α$ and Ni filter. The tested samples all display a c-axis spacing of 12.7 Å, which indicates a monolayer of water molecules. Bearing in mind that an acetamide molecule has maximum thickness of 3.5 Å and that the residual interlayer spacing is $Δ = 12.7 − 9.6 = 3.1$ Å, it appears that the organic molecule cannot enter into the interlayer spacing. However, Mortland and Tahoun (1966) claim that they have intercalated acetamide between the layers of a montmorillonite with a 12.6 Å c-axis spacing. To support this statement, they refer to the works of Brindley and Hoffmann (1962), as well as Greene-Kelly (1956) who interpret the decrease of the interlayer spacing by postulating a 'collapse' or incorporation effect of the molecules into the hexagonal sites of the silicic surfaces, and which they refer to as 'keying'. For this reason, we studied acetamide–montmorillonite complexes wholly dehydrated over P$_2$O$_5$. Under these particular conditions, the c-axis spacing between the layers of Na$^+$ montmorillonite is about 9.8 Å. Yet, owing to the difficulties attendant on a study concerned with oriented aggregates (as rehydration in air is very rapid), we performed new analysis on powders, according to Debye and Scherrer's method. The samples introduced in Lindemann's capillaries, are left to stand for 30 days over P$_2$O$_5$, the tube being quickly sealed just prior to analysis. Under these conditions, the c-axis spacing of the acetamide–Na$^+$ montmorillonite complexes shifts to about 10 Å. Because, in this case, the interlayer spacing is fully inadequate to accept an acetamide molecule, one may safely conclude that the organic molecule is retained on the external surface.

ADSORPTION MECHANISMS OF ACETAMIDE

The study of the adsorption of acetamide on to clays thus allowed clarification of a number of points. Under our working conditions, i.e. at low aqueous concentrations and without imposing a pH on the solution: (i) the acetamide is irreversibly absorbed at the external surface of the clay particles; (ii) the adsorption involves the existence of neutral and charged (protonated) molecules; (iii) these two types of molecules lead to two kinds of adsorption: chemisorption for protonated molecules and physical adsorption for neutral molecules; (iv) the quantity chemisorbed depends on the polarizing power of the exchangeable cation; (v) the amount retained through physical adsorption is a more substantial one—it decreases strongly as temperature increases; (vi) acetamide adsorption on to kaolinite is of the same order of magnitude.

At this point, consideration should be given first to the 'intense' adsorption, which displays the character of a chemisorption, and then the 'labile' or physical adsorption.
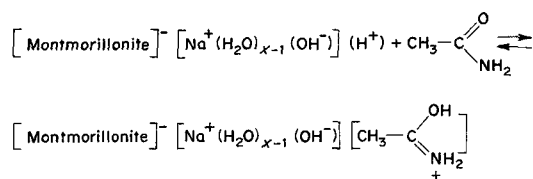
Chemisorption

In this case, acetamide is present in a cationic (protonated) form on the external surface of the clay crystallite. The amount retained is a function of the polarizing power of the exchangeable cation. Evidence has been provided for a linear relationship between these two parameters (Figure 6). The comparison of the quantities adsorbed to the external cationic exchange sites of montmorillonite, which amounts to ca. 20% of the net exchange capacity (88 mequiv. g/100 g) i.e. approximately 17 mequiv./100 g of mineral, shows that they correspond roughly to 1/3 of the CEC of sodium montmorillonite, 1/5 for Cs$^+$ montmorillonite and 1/2 for Li$^+$ montmorillonite. The external exchange capacity is therefore far from being exhausted, even in the case of excess acetamide in solution. Therefore it is likely that the uptake does not originate from an ionic exchange between protonated molecules of acetamide and exchangeable cations on the external surfaces of montmorillonite. In another connection, we have to account for the presence of protonated molecules of acetamide in a nearly neutral aqueous medium. Indeed, the existence of such a molecule in such a solution is not realistic.

This phenomenon may be explained by Fripiat's (1965) and Mortland's (1968, 1971) works, which show that the dissociation of water molecules on contact with exchangeable metallic cations brings about proton formation. This hydrolysis reaction obviously depends on the polarizing power of the cation referred to, and may be written as follows:

$$[Me(H_2O)_x]^{n+} \rightleftharpoons [Me\,OH\,(H_2O)_{x-1}]^{(n-1)} + H^+.$$

The presence of these protons on the surface gives rise to the surface acidity of montmorillonite. There is a relationship between the exchangeable cation and the ability of montmorillonite to donate protons to the adsorbed molecules (Mortland and Raman, 1968; Frenkel, 1974). The greater the polarizing ability of

the cation, the stronger are the acid sites and hence the dissociation of the water. So, if an acetamide molecule is close to the surface, it undergoes protonation. The resulting cation will be retained on to the clay crystallite by ionic bonding. Such a reaction may be written as follows.

$$\left[\text{Montmorillonite}\right]^{-} \left[\text{Na}^{+}(\text{H}_2\text{O})_{x-1}\,(\text{OH}^{-})\right](\text{H}^{+}) + \text{CH}_3-\text{C}\begin{smallmatrix} \text{O} \\ \text{NH}_2 \end{smallmatrix} \rightleftharpoons$$

$$\left[\text{Montmorillonite}\right]^{-} \left[\text{Na}^{+}(\text{H}_2\text{O})_{x-1}\,(\text{OH}^{-})\right]\left[\text{CH}_3-\text{C}\begin{smallmatrix} \text{OH} \\ \text{NH}_2 \\ + \end{smallmatrix}\right]$$

It seems reasonable to postulate that this reaction essentially takes place on the edge surfaces of the clay crystal where the 'broken bonds' of the silica–alumina units give rise to a maximum of unsatisfied charges, balanced by adsorbed cations. The amount of amide retained depends on the quantity of protons formed initially and, consequently, on the nature of the exchangeable cation. It follows that the quantity of protons thus transferred on the organic molecules cannot be very high. Hence, it is apparent that a saturation of the edge surface cannot be attained. In other words, such a mechanism fits the results recorded with kaolinite.

Physical adsorption

The experimental results show that a physical adsorption of neutral molecules must be superimposed on the intense adsorption which has been described. This physical adsorption takes place through the formation of hydrogen bonds between the neutral acetamide molecules on the one hand, and the protonated molecules on the surface of the mineral, on the other.

The following schemes are possible: (i) adsorption on the edges (Figure 9); (ii) adsorption on the basal planes (Figure 10). The presence of water bridges between the organic molecule and the mineral accounts for the decrease of physical adsorption after prior drying of the clay and as the adsorption temperature increases. The mobility of the water molecules is enhanced to such an extent that no bridge linkages may be created. The low hydration capacity
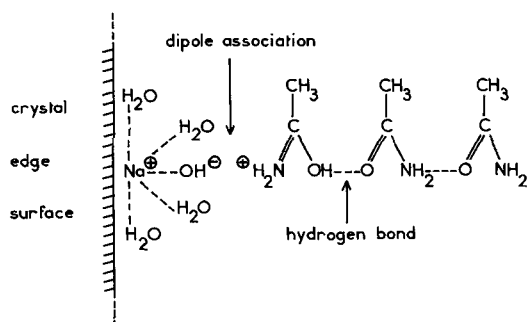

Figure 9. Adsorption mechanism of acetamide molecules on to the edge surface of montmorillonite particles.
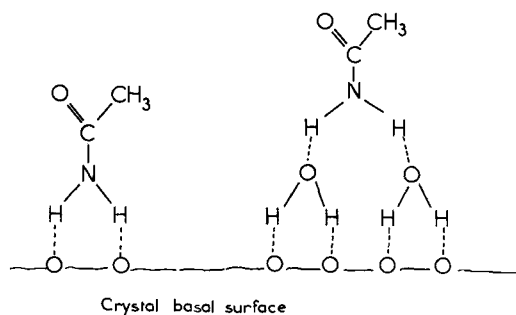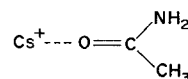

Crystal basal surface

Figure 10. Adsorption mechanism of acetamide molecules on to the basal surface of montmorillonite particles.

of the cesium cation allows a direct coordination of the organic molecule with the cation located on the edge surface:

$$\text{Cs}^{+}\text{---}\,\text{O}=\text{C}\begin{smallmatrix} \text{NH}_2 \\ \text{CH}_3 \end{smallmatrix}$$

Such a coordination phenomenon was reported by Mortland (1966). However, it is probably a boundary manifestation, in so far as it involves the presence of a weakly hydrated and bulky cation. This interaction is observed on the infrared spectrum of acetamide–Cs^{+} montmorillonite. The levels of the 'intense' retention are identical for both montmorillonite and kaolinite. Yet, if the exchange capacity of this mineral is considered (3 mequiv./100 g) the amount of bound acetamide is comparatively high (2.2 mequiv./100 g). A difference in surface area between these minerals may not be an explanation for this phenomenon, the value for montmorillonite being much higher than that for kaolinite. An explanation originates from the low water adsorption capacity of kaolinite. In fact, according to Mortland (1971), the lower the hydration, the higher is the surface 'acidity' and, consequently, the higher the quantity of bound acetamide.

It can be asserted that the adsorption of the acetamide molecule on to montmorillonite at room temperature is a complex phenomenon, involving at least three separate mechanisms of unequal importance. As the temperature increases, the protonation mechanism remains the only one, owing to the poor stability of the physical adsorption involving hydrogen bonding and water bridges.

THE MECHANISM OF ADSORPTION OF POLYACRYLAMIDES ON TO CLAYS

The studies performed thus far in the area of polyacrylamide adsorption are primarily concerned with technological problems arising from the use of this compound in petroleum applications. The main parameters contributing to an 'oil field' application of these polymers are: (i) the nature and the quality of the polymer. They are determined both by the molecular weights and by the degree of hydrolysis. Inter-

esting results are obtained with molecular weights above 3×10^6 when the degree of hydrolysis is kept between 10 and 30%; (ii) the properties of the solution. The concentration, the pH and the salt content are essential factors of the waterflooding efficiency. Polymer concentrations below 0.5 g/l are used, the salt content is largely variable, depending on the origin of the water; (iii) the mineral environment. The nature and the porosity of the rocks playing a significant part are very variable.

It should be remembered that two hypotheses have been proposed to explain the retention phenomenon on rocks. According to some authors, it is a matter of mechanical trapping ('filtration' by the medium); others believe that an adsorption has to be taken into account. In the present case (dispersed clays), the phenomenon can only be an adsorption, as the medium involved does not contain any 'pores' capable of retaining the polymer. Michaels and Morelos (1955) suggested three mechanisms accounting for the fixation of polyelectrolytes on to a clay (kaolinite): (i) an anionic exchange between the surface hydroxyls of the mineral and the carboxylic anions of the polymer; (ii) the formation of hydrogen bonds between the surface hydroxyls and the $C=O$ groups of the polymer; (iii) the establishment of bridges involving divalent ions, originating from electrostatic forces. An additional mechanism reported by Mortland (1966), Tahoun and Mortland (1966) and supported by our own investigations relating to acetamide fixation may be proposed: the protonation of amidic groups on the edge surface of clay crystals, involving a retention through electrostatic forces. Still, owing to the dilution of the solutions in this study, the creation of a direct interaction, such as coordination to exchangeable cations, is not realistic since this type of bonding is created only in the absence of or in the presence of very small quantities of water. The adsorption data currently reported allow the assumption that polyacrylamides are chiefly adsorbed by clays in rocks. Chauveteau (1973) points to a polymer retention of 0.11 mg/g in the case of an clayey sandstone, and 2 mg/g for pure clay. Assuming a 5–6% proportion of clay in the sandstone, the value of 0.10 mg/g is attained if adsorption is taken into account merely on to the clay fraction of that rock. Zavorokhina and Kaganskaya (1967) reported a polyacrylamide retention of 1.3–2 mg/g clay. Yet, the nature of the clays (a mixture of hydromica and montmorillonite) and the degree of polyacrylamide hydrolysis—which probably exceeds 50% in view of the polymer preparation—were not stated precisely. That is the reason why, in our study, the adsorption isotherms of clearly defined polymers were determined without adjusting the pH of the solution (pH $\simeq$ 7.5). The isotherms were obtained after unequivocal determination of the bound polymer. The procedure was similar to that used in the acetamide–montmorillonite investigation: 1 g of montmorillonite was dispersed in 20 ml of polymer solution

(0.1–0.8 g/l), stirred for 24 hr and washed three times with distilled water. After oven-drying at 60°C, the amount of adsorbed complex is determined according to the micro-Kjeldahl method, taking the hydration of the material into account. In this way, reliable estimates of the quantity of polymer adsorbed on to the mineral may be obtained, provided the procedure has been previously standardized.

Just like the case of acetamide adsorption on to montmorillonite, it appeared necessary as a first step to verify the irreversibility of the adsorption. The amount retained has therefore been followed as a function of the number of washings. As with acetamide, the weakly retained excess polyacrylamide is wholly removed from the mineral after the third washing, the quantity determined remaining constant thereafter whatever the number of subsequent washings. The polyacrylamide retention is therefore irreversible under these conditions: the adsorbed macromolecule is not removed by subsequent treatments.

Effect of the degree of hydrolysis

A first run of experiments was carried out on a set of three polyacrylamide samples supplied by S.E.P.P.I.C. Ltd (France), displaying similar polymer weights of about 11×10^6 with a 'narrow' distribution around the mean value. The degrees of hydrolysis are 15, 20 and 25% respectively. The three resulting isotherms are plotted in Figure 11. The adsorption appears slightly stronger for the polymer with the highest degree of hydrolysis, the discrepancy assuming significant values at low concentrations. Still, the maximum adsorption remains nearly identical for the three polymers, and ranges from 2.5 to 3 mg/g, the least hydrolyzed polymer having not yet fully attained the limiting value. Concentrated solutions were not investigated because viscosity made a total dispersion of the clay impossible even after stirring vigorously for 24 hr.

Effect of the molecular weight
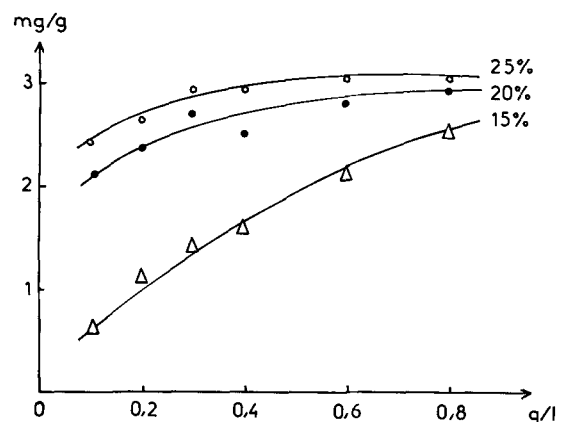
The study was centered on three products provided

Figure 11. Adsorption isotherms for polyacrylamide on Na-montmorillonite at 20°C: influence of the degree of hydrolysis of the polymer (mol. wt = 11×10^6).

by the same supplier, and displaying the same degree of hydrolysis (20%), but with polymer weights of 6×10^6, 7.5×10^6 and 11×10^6, respectively. The adsorption curves for these three polymers are represented in Figure 12. Despite a similarity in appearance, the curves are inverted for concentrations above 0.3 g/l. In fact, the polymer with the lowest molecular weight (6×10^6) displays a slightly higher adsorption than the polymer with an intermediate molecular weight (7.5×10^6). The discrepancies are not particularly significant, as the adsorption limits range from 2.4 to 2.8 mg/g mineral.

Effect of the adsorption temperature

An investigation of the adsorption on to montmorillonite, but restricted to one species (hydrolysis = 20%, mol. wt = 11×10^6), was carried out at 70°C. No disagreement with the values obtained at room temperature has been noted, within experimental error. The temperature seems to make hardly any contribution to the adsorption of polyacrylamide on to montmorillonite.

The various samples were investigated after the adsorption by means of X-ray powder diffraction. In the case of samples kept for 15 days in a desiccator with a relative humidity of 52% (NaHSO$_4$ saturated solution), the basal spacing is 12.7 Å, the diffractogram being identical to that of a sodium montmorillonite submitted to the same conditions. This result seems logical since the macromolecular chain displays such dimensions that a keying into the interlayer spacing is most unlikely to occur. In addition, it seemed attractive to establish the diffraction diagrams in the case of clay polymer complexes dried over P$_2$O$_5$ (30 days). In this case, the c-axis spacing is as low as 9.9 Å. Not only is there no intercalation of small macromolecular chain-elements, but also the layer is not 'blocked' by the polymer and the interlayer water may leak out, allowing an almost complete dehydration of the montmorillonite.

The previous experiments thus provide attractive data concerning the quantitative adsorption of polyacrylamide. It is a comparatively restricted one (3 mg/g at the utmost), the limit being not affected by a rise in temperature. In addition, the adsorption occurs on to the external surfaces of the clay particle in the same way as for acetamide. From the quantity of polymer adsorbed it appears that the surface is probably not saturated. This is confirmed experimentally by an easy displacement of interlayer water from the clay and by the wide surface available per molecule of polymer. In fact, assuming the quantity of bound polymer to be 3×10^{14} molecules (3 mg) of polyacrylamide (mol. wt = 6×10^6) per gram of clay, the area available per molecule of polymer is considerably superior to 10,000 nm^2, the surface area of montmorillonite being equal to 16.5 m^2/g. On the other hand, the increase of the amount adsorbed, as the degree of hydrolysis increases, seems to denote that the accessibility to the surface depends on the

size of the molecule. Indeed, Michaels (1954) showed that the polyacrylamide molecule tends to take the conformation of an extended chain as the degree of hydrolysis increases, the lateral bulkiness of the molecule becoming lower (Figure 13). The adsorption depends therefore on the steric hindrance of the macromolecule. Lastly, the negative charge of the macromolecule is stronger for a high degree of hydrolysis. This charge variation is apt to be involved in the fixation mechanism. Moreover, the molecular weight seems to be comparatively little related to the adsorption. It may be assumed that, for such high molecular weights, a slight difference in molecular weight exerts but a small effect upon the configuration of the molecule and, consequently, on the adsorption. The results prove to be similar to those obtained with acetamide. The 'chemisorption' of acetamide on to Na$^+$ montmorillonite also involves a maximum adsorption of 3 mg/g. In reality, this result was obtained at a higher concentration (2.5 g of acetamide per liter, instead of 0.8 g/l). In the case of acetamide, it may be assumed that this value corresponds to the saturation of all protonated sites on the edge surfaces of the clay particle. As for the polymer, owing to its mass and volume, one may assume that saturation cannot be attained. Furthermore, taking into account the flocculating properties of polyacrylamides, one comes to the conclusion that the polymer molecule becomes adsorbed, not on to one particle, but on to several. Thus, an aggregation between several macromolecules and several particles has to be considered, involving a significant decrease of the bonding possibilities between the molecule and the protonated sites of the clay crystals.

Such an assembly points to the restricted effect of the molecular weight of the polymer. The size of an aggregate therefore would be uniquely dependent on the degree of hydrolysis (which keeps down the number of bondings likely to appear between the polymer and the surface) and on the power of the bonds. As the degree of hydrolysis increases, the relative lengthening of the macromolecule changes. The
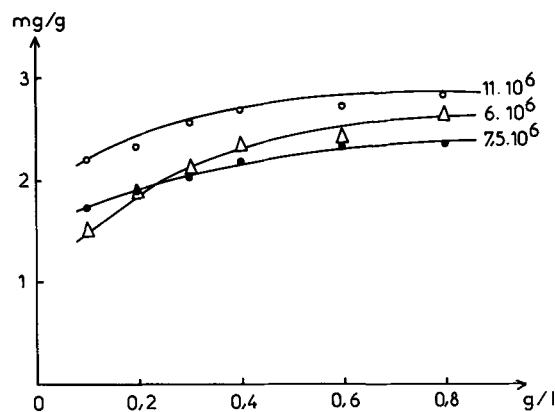

Figure 12. Adsorption isotherms for polyacrylamide on Na-montmorillonite at 20°C: influence of the molecular weight of the polymer (20% hydrolysis).

Effect of hydrolysis on polyacrylamide character

slightly hydrolyzed
non-ionic (isoelectric)
tightly coiled chain

33% hydrolyzed
anionic
extended chain

67% hydrolyzed
strongly anionic
extended chain

After Michaels (1954)

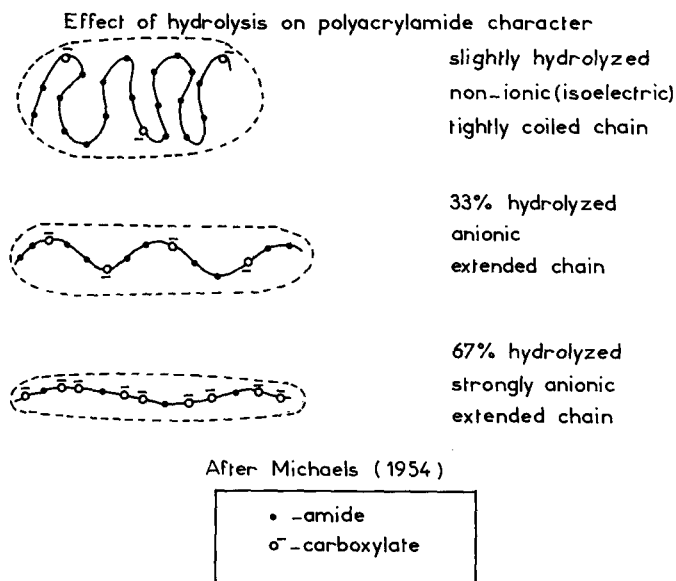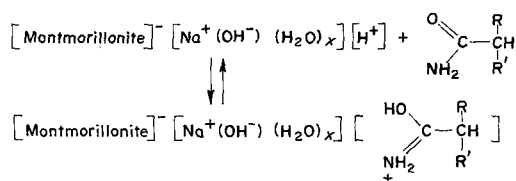| • –amide |
| σ⁻ –carboxylate |

Figure 13. Effect of hydrolysis on polyacrylamide character in aqueous solution.

volume between the crystallites of an aggregate is, accordingly, filled in a different way by the quantity of polymer in relation to the mineral. In effect, the polymer exhibits such a strong affinity towards the mineral, that a flocculation of montmorillonite can be observed, even for very small quantities of polymer. The creation of chemical bonds between both compounds must therefore be considered. Comparing the behavior of polyacrylamide to the behavior of acetamide under similar conditions (which preclude the adsorption of carboxylic acids), an adsorption mechanism of the same kind may be advanced: protonation of certain amide functions and adsorption through ionic bonding. Using R and R′ to designate macromolecular chains, this mechanism can be represented:

$$[\text{Montmorillonite}]^- \; [\text{Na}^+ (\text{OH}^-) \; (\text{H}_2\text{O})_x] \, [\text{H}^+] \; + \; \overset{O}{\underset{NH_2}{\overset{\diagdown}{C}}} - \overset{R}{\underset{R'}{\overset{|}{C}H}}$$

$$[\text{Montmorillonite}]^- \; [\text{Na}^+ (\text{OH}^-) \; (\text{H}_2\text{O})_x] \; \left[\; \overset{HO}{\underset{\underset{+}{NH_2}}{\overset{\diagdown}{C}}} - \overset{R}{\underset{R'}{\overset{|}{C}H}} \; \right]$$

This mechanism can be clearly generalized to other clays, the amounts retained depending in each case on the edge surfaces available for polymer adsorption. Water bridges may be superimposed on the protonation mechanism of adsorption. This contribution depends on the hydration of the complex (Zavorokhina and Kaganskaya, 1967). It is probably a small one, inasmuch as the weight of polymer adsorbed is little affected by the temperature. Lastly, according to Ruehrwein and Ward (1952), a polymer uptake through ionic exchange may be assumed. In the present case, a simple calculation shows that the quantity of polyacrylamide adsorbed is inferior to the anionic exchange capacity by a factor of about 30.

In another connection, when the pH of the suspensions is approximately 5, the number of carboxylate functions on the polymer is very low. The exchange of structural anions (probably OH) by carboxylate functions must also be low, although the positive double layer of clay micelles is closely packed in acid medium (van Olphen, 1963). In the same way, the geometry and the size of the polymer molecules do not favor the ionic exchange (Grim, 1968). Accordingly, it is difficult, if not impossible, to determine the contribution of the ionic exchange during the adsorption.

Finally, the polarizing power of the exchangeable cations of the clay is the most significant factor in the adsorption mechanism, and determines the proton donating ability of the mineral surface.

GENERAL CONCLUSIONS

The main conclusions resulting from the present work are:

(1) The adsorption of polyacrylamide (an anionic polyelectrolyte) on to clays in weakly acid medium, probably corresponds to a 'chemisorption'. The polarization of the water molecules on contact with the exchangeable cations of the clay generates protons on the edge surface of the clay crystallites. The polymer is adsorbed on to these protonated sites after a transfer of hydrogen to the amide groups has occurred. This result is postulated from another study which was carried out under the same conditions with acetamide.

(2) The interaction between the polyacrylamide and the clay micelles is attended by a coflocculation, characterized by the formation of polymer bridges between several mineral particles.

(3) In the case of coflocculates with high hydration ratios, a physical adsorption can be superimposed on the 'chemisorption'.

(4) The adsorption depends on the characteristics on the polymer; it increases as a function of the degree of hydrolysis, i.e. varies as a function of the configuration and the volume of the solvated macromolecule.

(5) The quantities of polymer and acetamide adsorbed through 'chemisorption' are small (3 mg/g).

(6) Nevertheless, the quantity of polyacrylamide irreversibly bound to the phyllite mineral is a significant one if we consider the use of the polymer in petroleum applications. Indeed, the experimental data lead to an adsorption of *ca.* 450 g of polymer per m^3 of a clayey sandstone with a 5% clay content. For an oil reservoir, the adsorption will lead to a loss of several thousand tons of polymer.

(7) The loss in polymer can be reduced to a minimum by using low concentrations of weakly hydrolyzed polyacrylamide.

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