

ACETAMIDE AND POLYACRYLAMIDE ADSORPTION ONTO CLAYS: INFLUENCE OF THE EXCHANGEABLE CATION AND THE SALINITY OF THE MEDIUM

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Abstract—The adsorption of acetamide and partly hydrolyzed polyacrylamides onto montmorillonite has been investigated with emphasis on the valency of the exchangeable cation of the clay and the ionic strength of the medium. A difference in the adsorption of acetamide from 3 mg/g to 0.6 mg/g was observed when a Na⁺-clay was changed to a Al³⁺-clay. For polyacrylamide, an opposite effect was observed, and the fixation increased from 3 mg/g (Na⁺-clay) to 18 mg/g (Al³⁺-clay). This difference in behavior may be accounted for by the decrease in adsorption sites due to partial flocculation in the presence of polyvalent cations (tactoid formation). Adsorption in a saline medium is two- to fivefold greater for diverse polymers and substantially less for acetamide (from 3.0 mg/g to 0.77 mg/g). An increase in the degree of hydrolysis of the polymer results in a significant increase in adsorption. In contrast, a change of molecular weight has practically no influence upon the adsorption ratio. The results obtained in saline medium may be explained by a size decrease of the macromolecules, allowing a closer approach to the surface of the mineral substrate, and by a chain lengthening as the degree of hydrolysis increases, induced by the electrostatic repulsions between the COO⁻ groups.

Key Words—Acetamide, Adsorption, Montmorillonite, Polyacrylamide, Saline Media.

INTRODUCTION

Stutzmann and Siffert (1977) showed that the fixation mechanism of partly hydrolyzed polyacrylamide onto clays in weakly acidic media is a chemisorption phenomenon. The anionic polyelectrolyte is sorbed exclusively on the external surface of the clay, where organic molecules undergo protonation and are retained by ionic interaction. Charge transfer apparently depends on the polarizing power of the exchangeable cation of the clay, and a linear relationship was found between the polarizing power of the alkali elements and the quantity of material sorbed. They also observed for acetamide two simultaneous types of sorption: (1) a strong, irreversible sorption involving a monolayer of chemisorbed molecules, and (2) a more extensive, but weaker sorption wherein molecules are retained by hydrogen bonding and are easily removed by gentle heating. Irreversible, or chemisorption of acetamide and polyacrylamide on montmorillonite was found to be low (about 3 mg/g) and to be dependent on the cation-exchange capacity (CEC) and the surface area of the mineral. The sorption of polyacrylamide is also related to the CONH₂/COO⁻ ratio, which determines the length of the carbon chain and the molecular weight, both of which control the accessibility of the organic molecule to the clay surface. Stutzmann and Siffert (1977) limited their investigation to alkali-exchanged montmorillonite. The present study is an extension of this work and emphasizes the role played by the valence of the exchangeable cation and by the ionic strength (salinity) of the medium. To demonstrate the interaction mechanism, sorption data for both acetamide and polyacrylamide have been obtained.

MATERIALS AND METHODS

A Greek montmorillonite supplied by the CECA Corporation (France) under the name "KL" was treated with 0.5 N HCl to remove iron-containing impurities. Purification and dispersion were then carried out by repeated leaching with a 1 N NaCl solution. Finally, the sodic clay was washed to remove the residual salt, and the <2- μ m fraction was separated by sedimentation. The purified Na-montmorillonite has a cation-exchange capacity of 90 meq/100 g and the following anhydrous chemical composition: SiO₂ = 57.55%, Al₂O₃ = 14.41%, Fe₂O₃ = 4.31%, MgO = 4.0%, TiO₂ = 0.36%, CaO = 0.61%, Na₂O = 1.67%, K₂O = 0.63%. The Na-montmorillonite has a basal spacing of 13.1 Å. Differential thermal analysis curves show clear endothermic peaks at about 150°, 650°, and 850°C.

To examine the effects of clays saturated with cations of different valencies, Ca-montmorillonite and Al-montmorillonite were prepared from the sodic clay by leaching with 1 N solutions of calcium and aluminum chloride. Excess salt was removed by washing with water. Acetamide, supplied by the Prolabo Corporation (Ref. 20055), and partly hydrolyzed polyacrylamide, supplied by the SEPPIC Corporation (France), were sorbed onto the Na-, Ca-, and Al-montmorillonites at pH 7 by bringing 20 ml of aqueous amide-solution into contact with 1 g of clay at room temperature for 24 hr. The clay was dried at 60°C after three successive washings with distilled water, thus retaining only the irreversibly fixed amide (Stutzmann and Siffert, 1977). The amount of acetamide and polyacrylamide sorbed on the clays was determined by a micro Kjeldahl method, after washing and centrifugation. The rheological behavior

of the polymer was tested using a Haake Rotovisco RV3 viscometer, with the N.V. measuring head.

INFLUENCE OF THE VALENCY OF THE EXCHANGEABLE CATION IN THE CLAY

Acetamide adsorption

According to Stutzmann and Siffert (1977) the adsorption of acetamide onto montmorillonites saturated with various monovalent cations (Na^+ , Li^+ , Cs^+) in neutral medium takes place exclusively on the edge surfaces of the clay particles, where the organic molecule undergoes protonation. A linear relationship exists between the adsorption maximum and the polarizing power of the interlayer cation in the clay.

The adsorption isotherms for acetamide shown in Figure 1 are L-type curves according to the nomenclature of Giles and MacEwan (1957) and are similar to those reported by Stutzmann and Siffert (1977). These data seem inconsistent with Stutzmann and Siffert's data in the case of univalent cations, and adsorption decreases as the polarizing power of the cation increases ($\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}$). This may be accounted for by considering the surface areas of the various montmorillonites. The specific surface area of Na-montmorillonite determined by the B.E.T. method is $80 \text{ m}^2/\text{g}$. An adsorption limit of 3 mg/g on the edge surfaces therefore corresponds to a monolayer of acetamide molecules. The lesser amounts adsorbed by Ca- and Al-saturated montmorillonites can only be explained by a reduction in external surface of the minerals caused by partial flocculation (tactoid formation). This result is supported by Stutzmann and Siffert's (1977) observation that acetamide-montmorillonite complexes thoroughly dehydrated over P_2O_5 display basal spacing of about 9.8 \AA . A concentrated amide medium and an acidic system are prerequisite for interlayer adsorption (Tahoun and Mortland, 1966). In addition, coordination of the metal cations in the clay generally involves dehydration of the complex.

Polyacrylamide adsorption

Isotherms for the adsorption of polyacrylamide A_2 polymer (M.W. = 6×10^6 ; degree of hydrolysis = 20%) onto Na-, Ca-, and Al-saturated montmorillonites are shown in Figure 2. Adsorption increases from univalent to divalent and to trivalent cation-saturated clay, confirming the adsorption mechanism reported by Stutzmann and Siffert (1977). The protonation of amidic functions assumes higher values in the presence of trivalent cations, which display a higher polarizing power. In contrast to acetamide adsorption, the edge surface of the clay crystallites is not saturated when polymers are involved, due to the existence of bridge linkages between the particles (flocculation of the system). Accordingly, the decrease in surface of the Ca- and Al-montmorillonites due to partial flocculation of

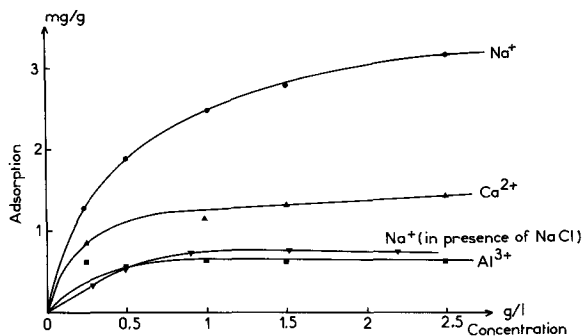


Figure 1. Acetamide adsorption isotherms on montmorillonite saturated with different cations.

the system is of little consequence. In addition, the flocculation of the polymer by polyvalent cations in the solution is not possible because cation exchange with the mineral can not take place under the conditions of the experiments. These results show that polyacrylamide adsorption increases in the presence of polyvalent cations which occur in the natural surroundings (especially Ca^{2+}).

INFLUENCE OF THE IONIC STRENGTH OF THE MEDIUM

The presence of salt in the secondary recovery of petroleum may affect the stability and configuration of polyacrylamides. Accordingly, the adsorption of acetamide and polyacrylamide has been studied at sodium chloride concentration of 100 g per liter.

Acetamide adsorption

The shape of the adsorption isotherm of this simple amide onto Na-saturated montmorillonite in presence of NaCl is shown in Figure 1. It is similar to the curve obtained in the absence of salt, but the adsorption limit (0.77 mg/g) is a great deal lower than that observed in the absence of salt (3.5 mg/g). This difference may be accounted for in several ways:

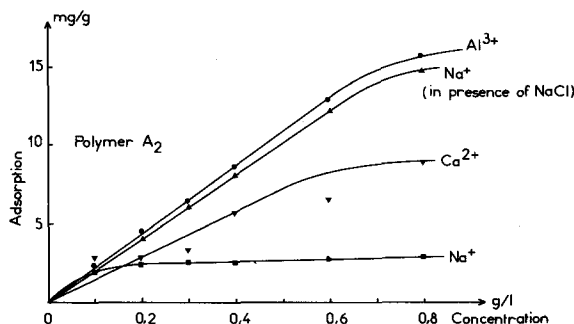


Figure 2. Polyacrylamide adsorption isotherms on montmorillonite saturated with different cations.

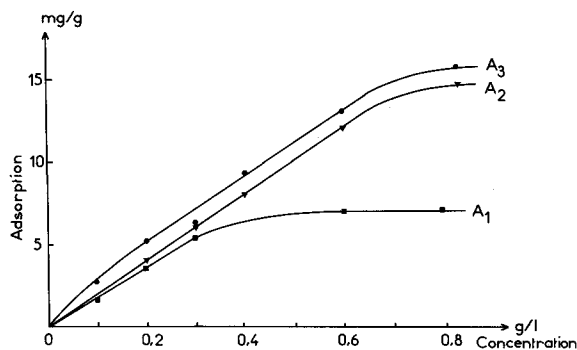
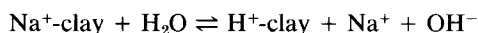


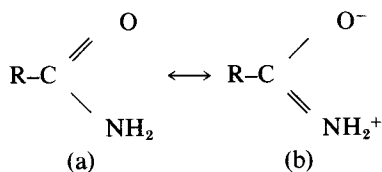
Figure 3. Polyacrylamide adsorption isotherms on Na⁺-montmorillonite in the presence of NaCl (100 g/liter); influence of the degree of hydrolysis.

Joint action of antagonistic ions. Sodic clay is strongly dissociated in the presence of water as follows:



The pH of the suspension is high (~9). In the presence of brine the dissociation is low, and the pH approximates to neutrality (pH ~ 7); Na⁺ ions are abundant and give rise to a so-called "card-house" flocculation structure (Van Olphen, 1977), arising from edge-to-edge or edge-to-face aggregation of clay crystallites. Here, the edge surface of the clay decreases significantly, resulting in a simultaneous drop in adsorption.

Action of the ionic strength. Salt in the medium may also influence either the acetamide molecular association (i.e., the configuration of the molecule) which involve hydrogen bonding (Kirrmann *et al.*, 1977) or the charge of the acetamide molecule. The acetamide molecule has a resonance structure



Structure (b) is favored in the vicinity of the surface of the mineral. However, the quaternary nitrogen atom may be solvated in saline medium by a high concentration of Cl⁻ ions, resulting in the formation of a screen of negative charges, which weakens the bonding between the acetamide molecule and the mineral carrier.

Each of these closely connected phenomena contributes in its own way to the lower acetamide adsorption.

Polyacrylamide adsorption

The influence of the degree of hydrolysis and the molecular weight of the organic macromolecule on the fixation in a saline medium were investigated separately. Adsorption isotherms for the following polymers are

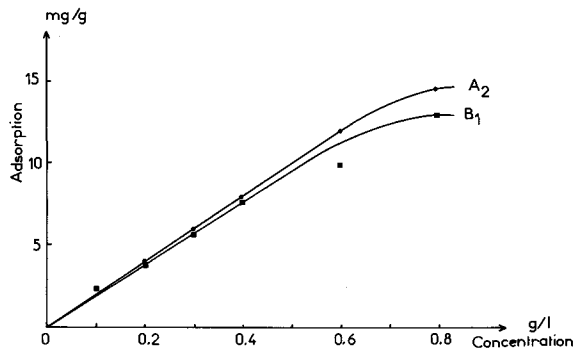


Figure 4. Polyacrylamide adsorption isotherms on Na⁺-montmorillonite; influence of the molecular weight.

shown in Figures 3 and 4. The degree of hydrolysis expresses the percentage of acidic functions carried by the polymer.

Polyacrylamide polymer	Molecular weight	Degree of hydrolysis
A ₁	11 × 10 ⁶	15%
A ₂	11 × 10 ⁶	20%
A ₃	11 × 10 ⁶	25%
B ₁	6 × 10 ⁶	20%

Influence of the degree of hydrolysis. For polymers A₁, A₂, and A₃, having the same molecular weight but different degrees of hydrolysis, it was found that the quantity adsorbed increases with the degree of hydrolysis and levels off at 25 to 30%.

Influence of the molecular weight. Adsorption isotherms for polymers A₂ and B₁, having the same degree of hydrolysis (20%) but having molecular weights of 11 × 10⁶ and 6 × 10⁶, respectively, are shown in Figure 4. The limit of adsorption slightly increases when the molecular weight of the polymer is doubled (1.7 mg/g of clay). This result is consistent with the observations of Stutzmann and Siffert (1977). From the adsorption data from polymer A₂ onto Na-saturated montmorillonite in presence of salt, shown in Figure 2, it is apparent that polymer adsorption is increased by a factor of 2 to 5 in the presence of NaCl. By dispersing the montmorillonite in an aqueous system, the polymer has been brought into contact with the clay. Moreover, direct determination of polymer fixation was carried out after washing the treated clay (redispersed in water, under the conditions used for treatment). Trapping into pores and polymer flocculation were thus avoided.

DISCUSSION

The ionic strength of the medium appears to be the most important factor influencing the ratio of polyacrylamide adsorption. Irrespective of the procedure and

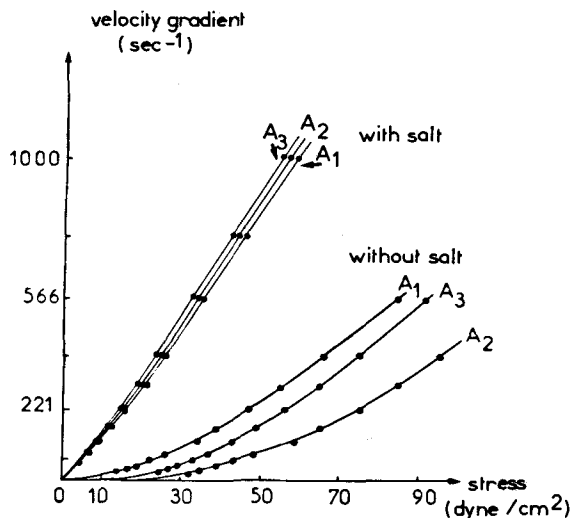


Figure 5. Rheological behavior of polyacrylamide solution in the absence and in the presence of NaCl (100 g/liter) for polymers A₁, A₂, and A₃ having the same molecular weight but different degrees of hydrolysis.

the nature of the polymer, the quantity of bound polymer is increased by a factor of 2 to 5 in the presence of NaCl (100 g/liter). On the other hand, the adsorption limit increases with the degree of polymer hydrolysis, with or without the presence of salt.

Several explanations of the overall increase in the quantity of polymer fixed in the presence of sodium chloride, may be considered. First, a polyelectrolyte may have (1) a coagulation effect on dispersed solids, due to a decrease in the electric double layer at the interface solution-dispersed clay particle (Van Olphen, 1977), and (2) a flocculating effect, resulting from polymer bridges between the mineral particles in suspension (Black *et al.*, 1966). The decrease in thickness of the double layer of the dispersed particles and in surface potential due to polyelectrolytes results generally in polymer adsorption and mineral-polymer heterocoagulation. The addition of salt brings about a slight decrease in the viscosity of the medium from a macroscopic point of view, but does not prevent coagulation and flocculation. The viscosity decrease may be caused both by a decrease in the size of the soluble organic macromolecule and by the disappearance of certain bridge linkages between the dispersed solid particles and the polymer. The former possibility has been verified by studying the influence of salinity on the viscosity of pure polymer solutions. From Figure 5, which shows the variation of shearing stress with velocity gradient for polymer solutions in the absence and in the presence of salt, it is apparent that the solutions display a pseudoplastic behavior. From the sharp drop in viscosity it may be inferred that sodium chloride induces

significant change in the macromolecules, i.e., the size of the coils decreases.

Sodium chloride also induces a so-called "salt effect" by increasing the activity coefficient γ_s of the solute (the polymer). The logarithm of γ_s is linearly related to the ionic strength of the medium as follows:

$$\log \gamma_s = K_m \mu, \quad \text{where } \mu = \text{ionic strength.}$$

The coefficient K_m is very high for carboxylic acids (Harned and Owen, 1958). In the present case a direct action of the salt on the configuration of the polyacrylamide molecule involving modification of the COO⁻/COOH ratio may be assumed. Thus, a decrease in the number of surface carboxylate groups induces a decrease in the relative length of the macromolecule, and hence an increase in the accessibility of the polymer to the surface of the mineral and in the quantity adsorbed.

The adsorption increase in the presence of NaCl may also be explained by a decrease in macromolecular bridges between the clay particles (viscosity decrease); the mineral particles are no longer connected, allowing a fixation of larger quantities of polymer (greater occupation of the adsorption sites). Black *et al.* (1966) used this argument to explain of the flocculating effect of polymers on dispersed matter. According to these authors, there is a limiting occupation value of the sites, beyond which a destabilization of the negatively charged colloids by the polyanions takes place.

It is more difficult to interpret the increase in the polymer fixation ratio when the degree of hydrolysis becomes higher. Nevertheless, it may be assumed that the action of the salt on the COO⁻/COOH ratio will be more pronounced for a strongly hydrolyzed macromolecule. In that case, the size decrease of the macromolecule would be more significant, involving the formation of low dimension coils which may draw most closely to the surface of the mineral. On the other hand, as the negative charge of the polyelectrolyte is lower, the polymer becomes more accessible to the clay micelle, which is itself negative. Finally, it should be remembered that a decrease in surface area of the mineral may occur in presence of salt, but the effect of this variation is likely to be low, because of the nonsaturation of the crystallite surfaces.

GENERAL CONCLUSIONS

The linear correlation between the quantity of acetamide adsorbed and the polarizing power of the exchangeable cation in the montmorillonite, established by Stutzmann and Siffert (1977) does not apply for cations with diverse valencies; here, the change of surface area of the mineral in the presence of polyvalent cations seems to be the predominant factor. For polyacrylamide adsorption, the coverage of clay micelles by the polymer is low; the surface charge is no longer predom-

inant; and adsorption increases as the polarizing power of the cation increases.

In the presence of salt, adsorption increases both for acetamide and polyacrylamide (up to 5 times for 25% hydrolyzed polyacrylamide). An increase in adsorption is observed also as the degree of hydrolysis of the polymer increases. Variation in molecular weight has little influence on adsorption. These results may be explained by steric reasons: as the ionic strength of the medium increases, the size of the molecule decreases, resulting in greater accessibility of the polymer at the surface of the mineral.

Therefore, if polyacrylamides are used to improve oil recovery, significant losses due to polymer adsorption onto the clay minerals of the surrounding rock are to be expected. Such losses will be even greater when the salinity of the medium is high.

ACKNOWLEDGMENTS

The authors are grateful to MM. Hemeury and Grangette for helpful discussions and to Elf-Aquitaine Society for financial assistance.

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(Received 8 September 1978; accepted 14 March 1979)

Резюме—Изучалась адсорбция ацетамида и частично гидролизированных полиакриламидов монтмориллонитом с упором на выяснение валентности обменного катиона глины и ионной силы среды. Наблюдались изменения в адсорбции ацетамида от 3 мг/г до 0,6 мг/г при замене Na^+ -глины на Al^{3+} -глину. Для полиакриламида наблюдалось противоположное явление: фиксация увеличивалась от 3 мг/г (Na^+ -глина) до 18 мг/г (Al^{3+} -глина). Это различие в поведении может быть объяснено уменьшением мест адсорбции из-за частичной флокуляции в присутствии поливалентных катионов (тактоидная формация). Адсорбция в соляной среде увеличивается от двух до пяти раз для разнородных полимеров и значительно меньше для ацетамида (от 3,0 мг/г до 0,77 мг/г). Увеличение в степени гидролиза полимеров вызывает значительное увеличение адсорбции. Наоборот, изменение молекулярного веса практически не влияет на адсорбцию. Результаты, полученные в соляной среде могут быть объяснены уменьшением размера макромолекул, что обеспечивает более тесный контакт с поверхностью минерального субстрата и удлинением цепей при увеличении степени гидролиза, вызванным электростатическим отталкиванием групп COO^- .

Reümee—Es wurde die Adsorption von Acetamid und teilweise hydrolysiertes Polyacrylamiden auf Montmorillonit untersucht, mit Nachdruck auf die Valenz des austauschbaren Ions in der Tonerde und auf die ionische Kraft der Umgebung. Ersetzt man Na^+ -Montmorillonit durch Al^{3+} -Montmorillonit so wird ein Acetamidadsorptionswert von 3 mg/g anstatt 0,6 mg/g gemessen. Falls Polyacrylamid eingesetzt wird, sind die Verhältnisse umgekehrt und die Adsorption steigt von 3 mg/g (Na^+ -Montmorillonit) bis 18 mg/g (Al^{3+} -Montmorillonit). Dieses verschiedenartige Verhalten erklärt man am Besten durch das Abnehmen von Adsorptionstellen, welches auf die teilweise Ausflockung in Gegenwart von mehrwertigen Kationen (Taktoidbildung) zurückzuführen ist. Die Adsorption in salzhaltiger Umgebung liegt zwei bis fünfmal höher für die verschiedene Polymere und bedeutend niedriger für Acetamid (von 3,0 mg/g bis 0,77 mg/g). Eine Zunahme des Polymerhydrolysegrades ist verbunden mit einer beträchtlichen Adsorptionserhöhung. Dagegen wirkt sich eine Molekulargewichtsänderung kaum auf das Adsorptionsverhältnis aus. Die in salzhaltiger Umgebung erzielten Ergebnisse erklärt man durch eine Grössenabnahme der Makromoleküle, welche ein enges Herannahen an die Oberfläche des Minerals ermöglicht und je nach dem der Hydrolysegrad zunimmt eine Kettenverlängerung, welche mit der elektrostatischen Abstoßung zwischen den COO^- Gruppen zusammenhängt.

Résumé—L'adsorption de l'acétamide et des polyacrylamides partiellement hydrolysés sur la montmorillonite a été étudiée en mettant l'accent sur l'influence de la valence du cation échangeable de l'argile et la force ionique du milieu. On observe une diminution de l'adsorption de l'acétamide de 3 mg/g à 0,6 mg/g lorsqu'on remplace une argile- Na^+ par une argile- Al^{3+} . Avec les polyacrylamides on assiste à un effet inverse; la fixation passe de 3 mg/g sur une argile- Na^+ à 18 mg/g sur une argile- Al^{3+} . Cette différence de comportement peut être expliquée par une diminution du nombre des sites d'adsorption due à une floculation partielle de l'argile en présence des cations polyvalents (formation de tactoïdes). En milieu salin, l'adsorption est deux à cinq fois plus élevée pour les différents polymères qu'en absence de sel; elle diminue par contre pour l'acétamide en présence de sel de 3 mg/g à 0,77 mg/g. Une augmentation du degré d'hydrolyse du polymère se traduit par une augmentation sensible de l'adsorption. Par contre, le poids moléculaire n'a pratiquement pas d'influence sur le taux d'adsorption. Les résultats obtenus en milieu salin s'expliquent par une réduction de la taille des macromolécules leur permettant une meilleure approche de la surface du substrat minéral et par un allongement des chaînes induite par les répulsions électrostatiques entre groupements COO^- lorsqu'on augmente le degré d'hydrolyse.