

Absorption and Desorption of Liquid Water by a Superabsorbent Polyelectrolyte: Role of Polymer on the Capacity for Absorption of a Ground

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ABSTRACT: To study the potentialities of a polyelectrolyte superabsorbent for the storage of water, we have studied a ground representative of the area of Haouz (area of Marrakesh, South of Morocco) in the presence of polymer. We sought the optimal proportions allowing the best retention of water by the mixture made up of the polymer and the ground and to prolong the storage period of water in the ground. We have also studied the effect of certain ions and the pH on the capacity for absorption of polymer. These ions can be naturally present in the ground or introduced by the means of manure and pesticides. The presence of polymer in the ground makes it possible to increase the capacity for absorption of the water by the ground, which can thus involve a saving in water while decreasing the frequency of irrigation and by reducing the water losses by the phenomena of evaporation and infiltration. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1541–1548, 2001

Key words: polymer; superabsorbent; freezing; ground; capacity for absorption

INTRODUCTION

The polymer superabsorbents (polyelectrolytes) can, by a phenomenon of absorption, retain high quantities of water liquidate (up to 1000 times their weight). These polymers inflate easily in the presence of liquid water or in salt solutions and give rise to transparent gel. This fundamental study is developed on a polymer superabsorbent able on the one hand to adsorb water vapor^{1–4} and on the other hand to absorb liquid water.⁵

The growth of the plants and their quality are mainly a function of the quantity of water stored

after the operation of irrigation.^{6,7} The mix design made up of the ground and freezing in pots in the presence of manure, showed that the maximum rate of absorption of water by the ground-freezing mixture is a function of the type of polymer used to prepare freezing.⁸

The polymer reaction on the surface of the ground is related to several factors such as the pH of the ground, the pH of absorptive water, and the presence of certain mono or divalent ions that are in the ground. We have studied the effect of certain parameters on the capacity for absorption of polymer out of water and its swelling. We have particularly analyzed the effect of the following:

- The pH of the medium, and thereby, the ionization level of the macromolecular chains. The pH affects the number of acid functions

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ionized (carried by the chains), consequently the number of loads located on the macromolecular chain. The pH of the aqueous solution used to inflate polymer is brought to the value wanted by addition of solution of NaOH or HCl.

- Content of ions mono and/or divalent, which affects the degree of reticulation, while adding to this solution a given quantity of ionizable salt, for example, NaCl, KCl, NH_4Cl . The positive loads coming from salt hiding-place between the negative charges carried by the polymeric chains and thus decrease the intensity of the force repulsive existing between the same load signs.
- The presence in the aqueous solution absorptive by polymer of certain divalent ions; in addition to the effect on the reticulation, those by an effect of complexing with the functional groups of the macromolecular chains cause their tightening and an additional reduction of absorption.

MATERIALS AND METHODS

Polymer

The studied polymer is a superabsorbent polyelectrolyte formed from acrylic acid. It is presented in the form of small spherical balls (diameter ranging between 10 and 100 μm .^{1,2}) These small spherical balls are formed by macromolecular chains dependent between them by covalent bonds. In liquid water, the polymer inflates instantaneously and quickly to form a transparent and soft gel. The water molecules are trapped between the macromolecular chains. If the water concentration believes, the chains lengthen and become increasingly flexible. When the quantity of water in the solution is raised, the chains are lengthened and the polymer reaches its balance of swelling which results from a compensation between the elastic force of recall due to the elasticity of the polymeric chains and the repelling powers existing between the groupings charged carried by the macromolecule.

Ground

The ground used in this study is representative of the area of Haouz (south of Morocco) provided by the specialized services of the Regional Office of Agricultural Development of Haouz for Mar-

Table I Physical and Chemical Characteristics of the Ground of the Area of Haouz to 30 cm of Depth

Composition of the Ground	Quantity
Clay	11.7%
Silt fine and coarse	49.3%
Sand fine and coarse	38.3%
pH	8.1
N	0.057%
C/N	3.5
K ₂ O	0.376%
P ₂ O ₅	0.692%
CaCO ₃	3.9%
Matter organic	0.56
C.E à 25°C mmh/cm	0.83
Salinity	1.31%
Humidite equivalent	16.35

rakesh. The physicochemical analyses of the ground were performed in the laboratories of this same office. We give in Table I the results of the analysis performed. The analysis of these results enables us to conclude that it is about a slightly basic ground, low in organic matter, presenting a good humification (significant report C/N), and rich in potassium and phosphorus.

We have realized a mineralogical study of the pleasure party of the ground by X-ray diffraction. The analysis of the spectrum of X-ray diffractions of a sample without preliminary processing reveals the existence of a mineral with 7 Å (kaolinite). It is characterized by the presence of the lines with 7.12 and 3.53 Å (Fig. 1). Minerals belonging to this family are characterized by lines with 7.12 and 3.53 Å which are preserved when one saturates mineral with the glycerol (which presents the property to inflate the layers of certain types of clay; Fig. 2), but disappears from the sample by heating to 450°C (during 4 h) without appearance of other lines (Fig. 3).

The spectrum of X-ray diffractions also shows the presence of a mineral with 10 Å characterized by the stability of the lines 9.9, 4.97, and 3.9 Å and which belongs to the family of the illite. The diagram of X-ray diffractions of this family has the effect of having a line with 10 Å which varies with the samples of 0.2 Å; this line becomes clearer on the diffractogram of a heated blade with 450°C (Fig. 3).

Also, we have noted the presence of a vermiculite which appears by the existence of an intense line with 14.4 Å (Fig. 1); this line is preserved

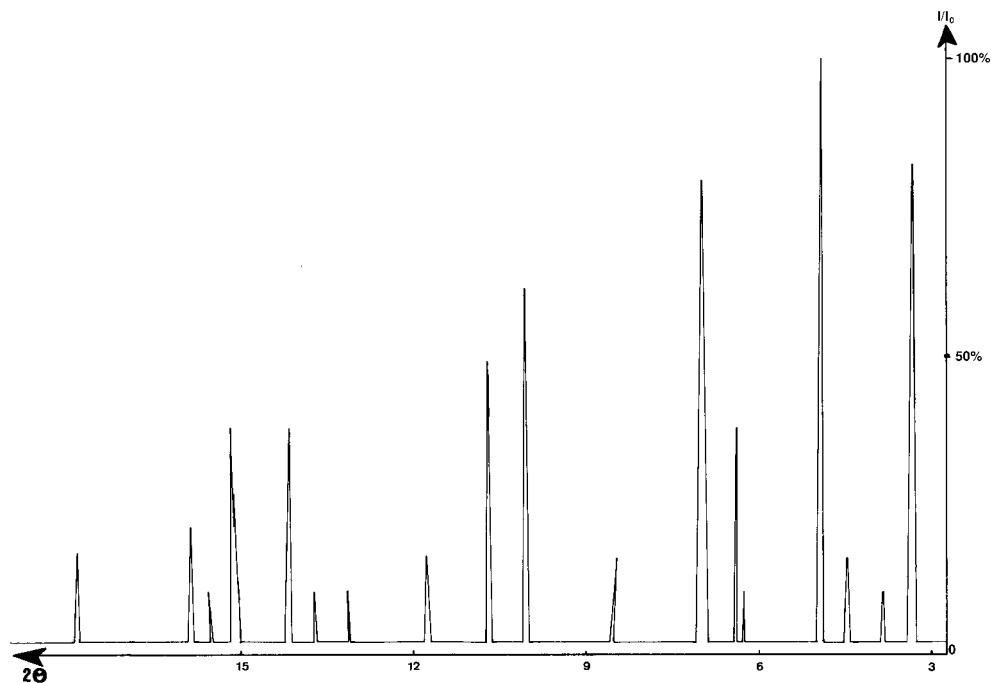


Figure 1 Spectrum of X-ray diffractions of a sample without preliminary processing.

after glycérolage (Fig. 2), but it disappears from mineral after heating (Fig. 3).

Swelling of the Polymer and the Ground

We studied the swelling of the polymer when it is put in liquid water, particularly its capacity for

absorption at the balance of swelling of the polymer and the effect of certain parameters on this capacity. We used two experimental techniques to compare the results obtained by these methods of measurement.

An opto-electronic device at the Laboratory of Electronics of Marrakesh⁹ was used to follow

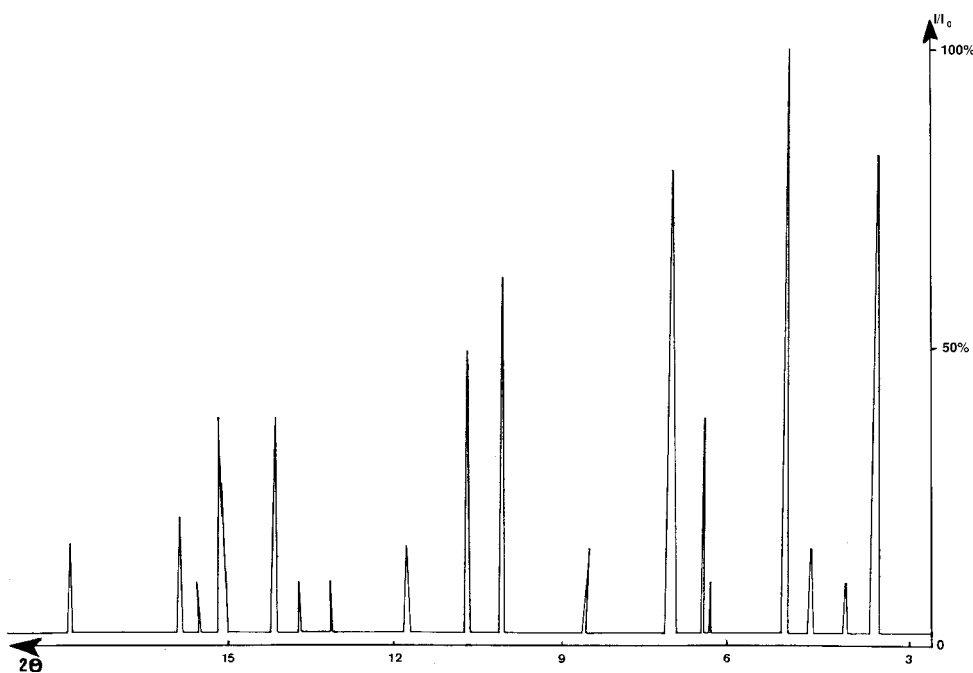


Figure 2 Spectrum of X-ray diffractions of a sample treated with glycerol.

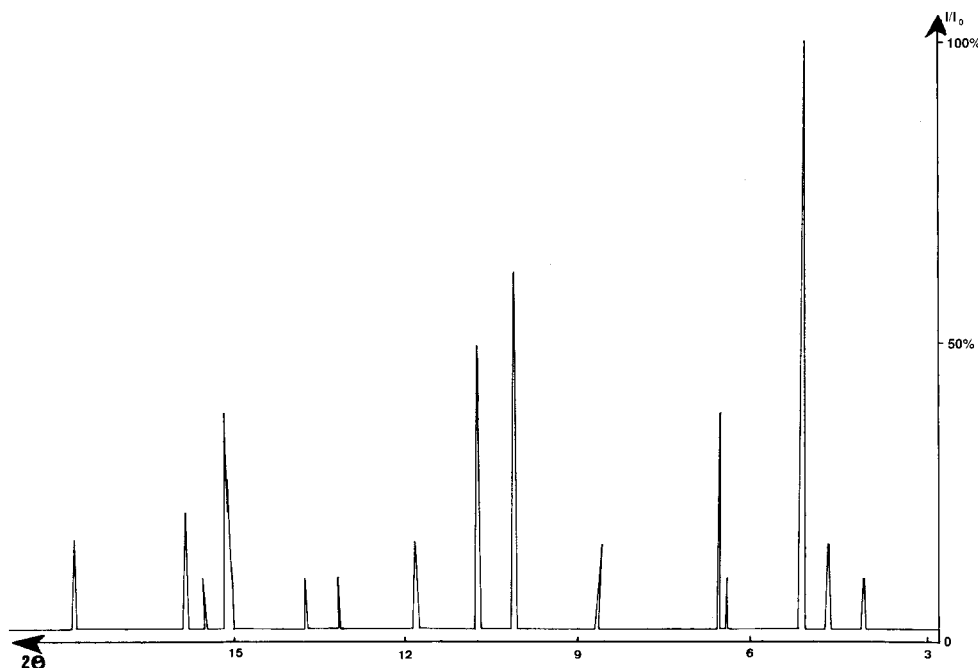


Figure 3 Spectrum of X-ray diffractions of a heated sample (450°C).

measurements of the intensity of the light transmitted by freezing in relation to the quantity of water absorptive by polymer. This system of measurement of transmission allows the automatic detection of the phases and the interfaces. The light transmitted by the polymer-water mixture then makes it possible to detect the interface water-freezing when the balance of swelling is established. The second experimental device is a tensiometer Lauda MESSGERAK-WERK MGB. The surface tension of freezing is followed in relation to the rate of absorption of the polymer and certain parameters.

To determine the quantity of maximum water absorptive by the ground (at a given temperature), the dry recomposed ground is introduced into a glass tank (1 × 3 cm) and water is gradually added until appearance and maintenance of liquid water on the surface of the sample is observed. By weighing the dry recomposed ground and recomposed ground saturated with water, we can deduce the rate of absorption maximum or saturation defined as being:

$$\theta = \frac{\text{mass water absorptive by the ground}}{\text{mass of the dry ground}}$$

We have also determined the rate of saturation of mixtures made up of recomposed ground and

polymer, for various percentages of polymer ranging between 1 g per kilogram of the ground and 10 g per kilogram of the ground, at ambient temperature and atmospheric pressure. The values of the rates of polymer used are selected after a bibliographical analysis. The studies performed on the application of the gel in the ground use rates ranging between 0.1 and 1.0%. The experiments showed that if the polymer is in the ground (no grain of polymer is on the surface of the ground), the polymer cannot absorb water. This is because of the low intensity of the electrostatic forces of repulsion between the sites charged.⁹ When the grains of polymer are on the surface of the ground, the polymer can inflate easily and forms a transparent gel.

RESULTS

Absorption of the Polymer

Influence of Salts

To determine the effect of salt (NaCl) on the capacity for absorption of the polymer, we followed the evolution of the surface tension of freezing (Fig. 4) and the light transmitted by freezing (Fig. 5) in relation to the quantity of absorptive water expressed by the report ($\theta = m_{\text{eau}}/m_{\text{poly}}$) for vari-

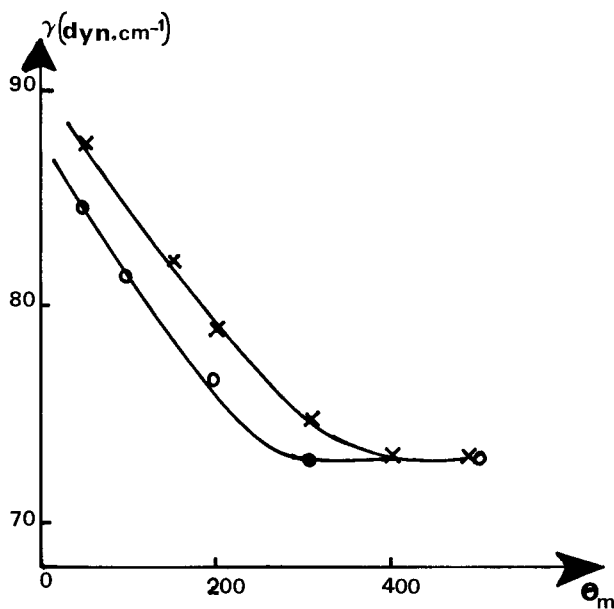


Figure 4 Evolution of the surface tension with the rate of absorption: pH = 7 and $T = 293$ K. ○, without NaCl; ×, 100 and 200 g/L of NaCl.

ous concentrations of NaCl in grams per liter of water at fixed pH and temperatures. The curves of Figure 4 are characterized by two parts: 1. a decreasing part where the surface tension of freezing decreases with the rate of absorption in a quasi-linear manner, and 2. the part where the

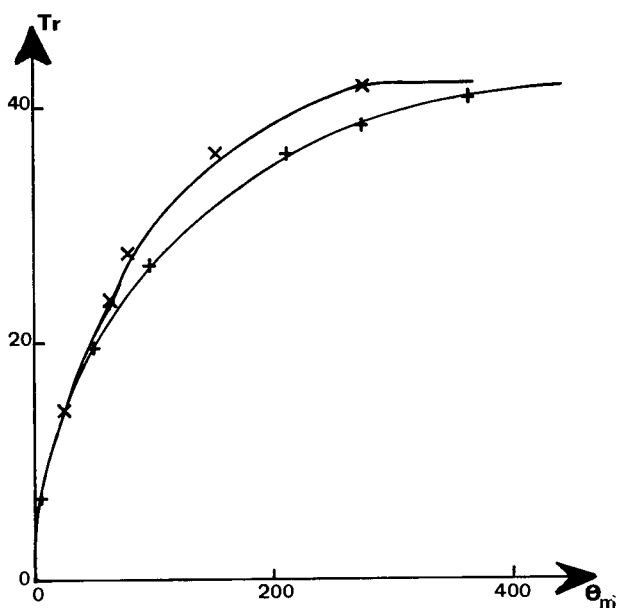


Figure 5 Variation of the transmission according to the rate of absorption: pH = 7 and $T = 293$ K. +, without NaCl; ×, 100 and 200 g/L of NaCl.

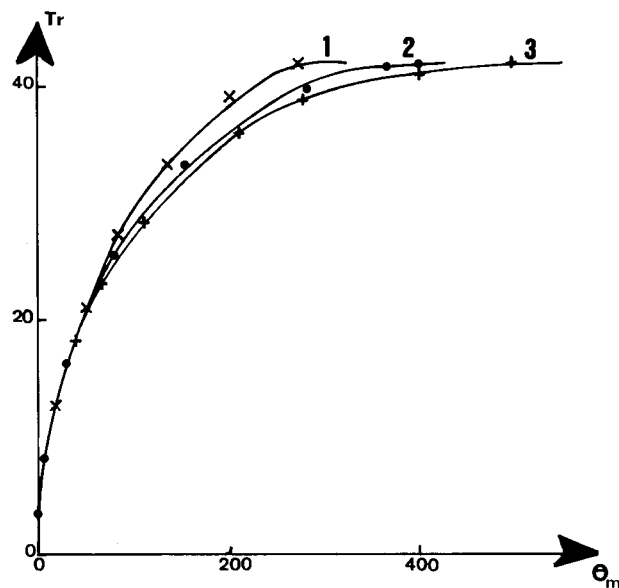


Figure 6 Variation of the transmission with the rate of absorption: $T = 293$ K. (1) pH = 2; (2) pH = 7; (3) pH = 12.

surface tension becomes independent of the quantity of water absorptive and equal to that of pure water.¹⁰

The presence of NaCl in the aqueous solution implies a lowering of the surface tension. This variation is practically constant until a rate of absorption equal to 300; it is also independent of the quantity of NaCl. The curves that correspond to 100 and 200 g/L are confused. For the curve without NaCl (pH = 7), the value of the tension becomes equal to that of water only for $\theta = 400$. However, for the values 100 and 200 g of NaCl, those become identical starting from $\theta = 275$.

The curves of transmission of light corresponding to various values of the concentration of NaCl (Fig. 5) are characterized by common part for the rates of absorption higher than 350 which is maintained with a constant value corresponding to that obtained under the same conditions of pure water¹⁰; this value is reached for various rates of absorption: from 450 per 0 g/L of NaCl to 290 per 100 and 200 g/L of NaCl.

Influence of pH

The analysis of the curves (Fig. 6) representing the variation of the light transmitted in relation to the rate of absorption for various values of pH (of the aqueous solution absorptive by polymer), showed that the influence of the pH appears especially in the interval of the rate of absorption

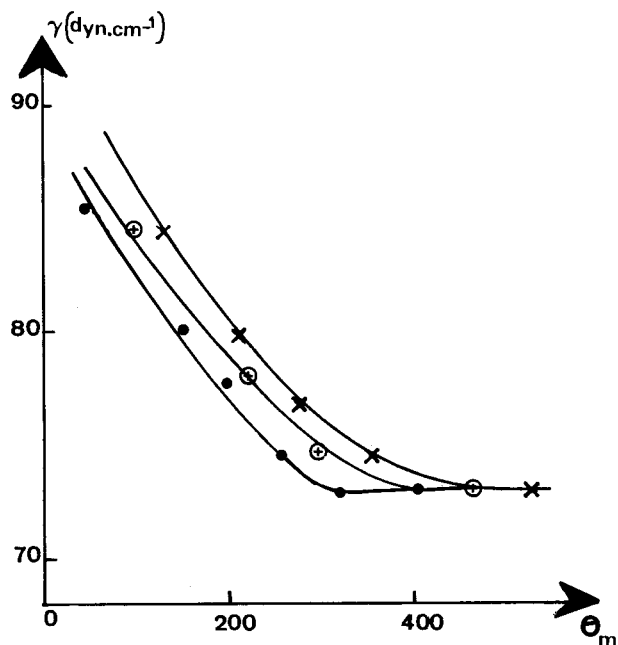


Figure 7 Evolution of the surface tension with the rate of absorption: $T = 293$ K. \times , pH = 2; \oplus , pH = 7; \bullet , pH = 12.

ranging between 50 and 400. When the pH of solution decreases, which corresponds to a reduction in the ionization level, the value of the transmission increases. We have also noted that the curves obtained reach the maximum value of transmission and become confused for different rates of absorption: (pH = 12, $\theta = 500$) (pH = 7, $\theta = 400$) (pH = 2, $\theta = 275$).

The results obtained by the measurement of the surface tension (Fig. 7) confirm those obtained previously (Fig. 6). Indeed, the curves obtained present two different parts. The first part indicates a reduction in the surface tension when the rate of absorption increases. In the second, the curves obtained are confused and the value of the surface tension is independent of the rate of absorption and the pH. For a same value of the rate of absorption the surface tension decreases when the value of the pH decreases. The increase in pH also involves an increase in the ionization level of freezing. In the same manner, it is noticed that the pH affects the maximum rate of absorption; when the value of the pH increases, the maximum rate of absorption increases: (pH = 2, $\theta = 300$) (pH = 7, $\theta = 400$) (pH = 12, $\theta = 500$).

Effect of the Presence of Ions

We present on Figures 8 and 9 the curves representing the evolution of the transmission of light

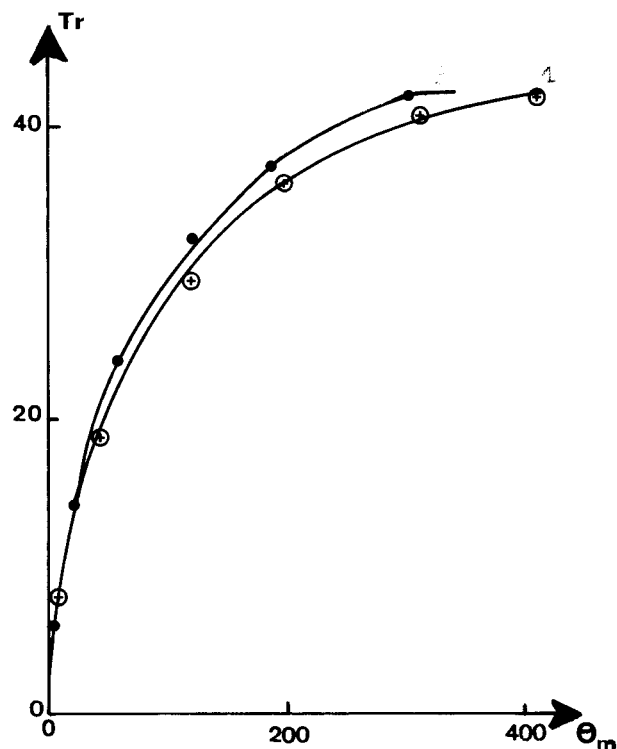


Figure 8 Effect of the divalent ions on the capacity for absorption: pH = 7. (1) Without addition of Ca^{2+} and Mg^{2+} ; (2) $[\text{Ca}^{2+}]$ or $[\text{Mg}^{2+}] = 0.2$ mol/L.

and the variation of the surface tension with the rate of absorption for various concentrations of NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} . The analysis of the

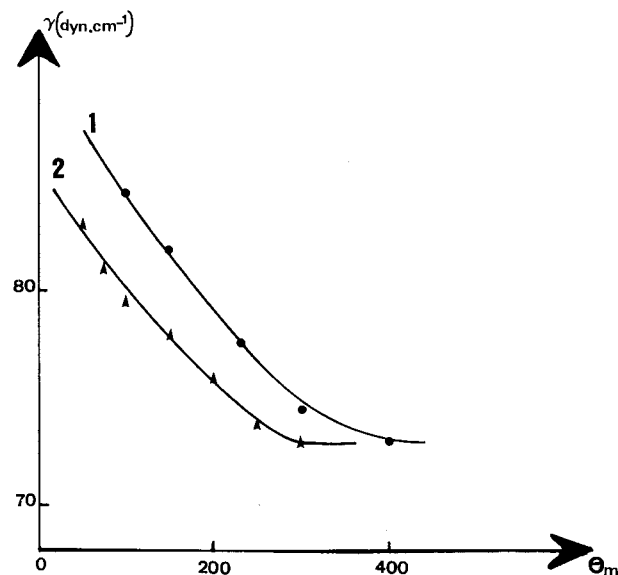


Figure 9 Effect of the mono-valent ions on the maximum capacity for absorption: pH = 7. (1) Without addition of NH_4^+ and K^+ ; (2) $[\text{NH}_4^+]$ or $[\text{K}^+] = 2.0$ mol/L.

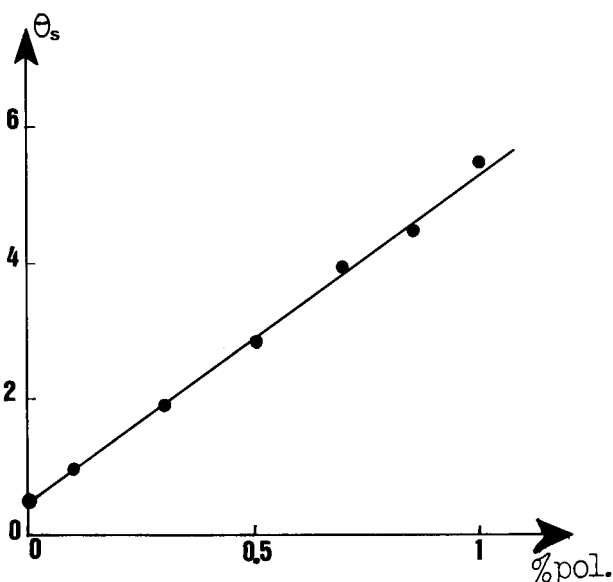


Figure 10 Evolution of the rate of saturation in relation to the quantity of polymer for a polymer/sol mixture, $T = 293$ K and $P = 1$ atm.

curves of Figures 8 and 9 makes it possible to conclude the following: the effect of Ca^{2+} and Mg^{2+} is identical and it is the same for NH_4^+ , K^+ ; and the effect of the mono-valent ions is accentuated more than the divalent ions, the rate of saturation passes from 400 (without addition of ions) to 300 for a concentration in Ca^{2+} or Mg^{2+} equal to 0.2 mol/L and to 300 for a concentration in NH_4^+ or K^+ of 2.0 mol/L.

Capacity for Absorption of the Ground Recomposed

We have determined the rate of saturation of the ground recomposed only without addition of polymer and of each one of its three separate fractions (sand, silt, and clay). The rate of saturation of the ground recomposed without addition of polymer is 0.5. However, this one passes from 0.23 for the sandy part to 0.33 for the muddy fraction and 0.7 for the clay fraction. The recomposed ground presents the same composition as an original ground; it is made up of 11.7% clay, 49.3% silt, and 38.3% sand.

We present on Figure 10 the evolution of the rate of saturation of mixture (polymer/sol) in relation to the quantity of polymer contained in the recomposed ground. The results show that the capacity for maximum absorption of the ground increases proportionally with the quantity of polymer contained in the ground. It is noted that

the rate of absorption is multiplied by a factor 10 for a percentage 1.0% of polymer. Calculation shows that the water mass absorbed by the mixture (polymer/sol), determined in experiments is the sum of the water masses absorbed by each separate product. A similar study was performed on each fraction constituting the ground (sand, silt, and clay). The results obtained are identical to those obtained in the case of the reconstituted ground. For the three examined fractions, we noted that when the polymer is on the surface of each fraction, its capacity for maximum absorption increases proportionally with the percentage of polymer.

DISCUSSION

In the study of the capacity for absorption of polymer, we noticed the following points. The reduction in the pH of the aqueous solution (absorptive by polymer) involves a reduction of the maximum rate of absorption. The macromolecular chains are ionizable in aqueous solution, then the polymer in aqueous solution gives rise to sites charged on the macromolecule. The presence of these localized loads causes a repulsion between the chains which induces an expansion of freezing (swelling). The increase in the pH of the aqueous solution supports the repulsive effects. Indeed, the number of sites in charge and consequently the rate of absorption believe with the pH. The use of a salt such as NaCl makes it possible for Na^+ to play an effect shielding between the sites charged of the macromolecule. The Na^+ ions come to fit between the polymeric chains and hiding-place between the loads carried by the macromolecule what minimizes the electrostatic repulsion¹¹ thus involving a reduction in the maximum rate of absorption.^{12,13}

The presence of the mono-valent ions K^+ and NH_4^+ induces (by effect shielding) a reduction in the capacity for absorption of polymer, as in the case of NaCl; only differs the of electrostatic forces ensuring the interaction ions-site charged. These forces of attraction depend not only on the load of the ion but also on its ray and its polarizing capacity. Given that the values of the rays of K^+ , NH_4^+ , and Na^+ are rather close:

$$r(\text{NH}_4^+) = 0,137 \text{ nm}; \quad r(\text{K}^+) = 0,149 \text{ nm};$$

$$r(\text{Na}^+) = 0,117 \text{ nm}$$

Their effect on the maximum capacity for absorption is identical; this one passes from 400 in the absence of these ions to 300 when $[\text{NH}_4^+] = [\text{Na}^+] = 2M$ and $[\text{Na}^+] = 1.7M$ (100 g of NaCl per liter of liquid water) for a ground with $\text{pH} = 7$.

The test with divalent ions showed that in addition to the shielding effect, it can have a formation of complexes¹⁴ which prevents the expansion of freezing; thus, the maximum rate of absorption decreases when the concentration of the divalent ions increases (Fig. 8). The rate of absorption passes from a value of 400 in the absence of the divalent ions (Fig. 8) to a value of 300 when the concentrations become equal to 0.2 mol/L.

The physicochemical analyses of the studied ground enabled us to conclude that it is about a slightly basic ground, low in organic matter, presenting a good humification (significant report C/N) and rich in potassium and phosphorus. The mineralogical study (by X-ray diffraction) of the pleasure party of the examined ground showed that the argillaceous fraction is indeed made up of three types of clays (illite, vermiculite, and kaolinite).

The study of the capacity for liquid water maximum absorption of the reconstituted ground (Fig. 10) showed that in the case of the mixture polymer/sol, the quantity of water absorbed increases proportionally with the polymer rate in the ground (of 2 to 10 times higher). Calculation shows that the absorbed water mass, determined in experiments is in fact only the sum of the water masses absorbed by each separate product constituting the mixture. With regard to the study performed on the three fractions constituting the ground (sand, silt, and clay) studied separately, we also noted that when the polymer is on the surface of any fraction, its capacity for absorption increases proportionally with the percentage of polymer.

CONCLUSION

The study of the capacity for liquid water absorption of the ground recomposed as well as those of the three fractions (clay, silt, and sand) in relation to the rate of polymer on the surface of each product, enabled us to note that the capacity for absorption of water by the ground increases with the percentage of polymer. The maximum rate of absorption of the ground is multiplied by a factor

10 for a polymer rate of 1.0%. The water molecules retained by the polymer are only trapped between the polymeric chains^{12,13} by the means of very weak connections (interaction ion-dipole) what can thus involve a better exchange of water between the ground and freezing.

The polymer under consideration in this study has interesting applications. It can be applied in the agricultural field insofar as it can increase the capacity for absorption of the ground water, which can thus induce savings in water by reducing the water losses by infiltration and evaporation and also by decreasing the frequency of irrigation. It can also improve the lifespan and the quality of plants in pots during their transport, or for the periods of holidays. It can also support the growth of transplanted plants while making it possible to preserve water on the ground for longer periods.

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