

The Adsorption of Water Vapor on Super Absorbent Product at Low Temperatures and Low Mass

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ABSTRACT: The adsorption isotherms of water vapor on super absorbent product have the same form of type III isotherm at ambient temperature with the hysteresis phenomena. For temperatures lower than ambient, the isotherms become deformed because of the chains effect. The polymer is characterized by a multilayer adsorption, which occurs before a full-course is complete. During adsorption reactions, the polymer undergoes rearrangement polymeric network, which results from a cooperative diffusion of the

water molecules and from a chain spacing followed by an expansion of the polymeric network. Three types of water molecules adsorbed on polymer were identified: strongly dependent water, adsorbed water, and the water only trapped between the macromolecular chains. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1450–1456, 2006

Key words: polymer; super absorbent; gel; adsorption; isotherm; isobar; heat; water; vapor

INTRODUCTION

Several studies related to the adsorption phenomenon of water vapor on certain polymers at high temperatures have been carried out.^{1–3} The studies related to that at low temperatures (<100°C) are fewer.^{4–6} In general, polymeric water is presented under two types on the basis of water adsorption: water related to macromolecular chains and free water. Indeed, the structure of adsorbed water remains intermediate between that of liquid and ice water. Generally, the organic polymers have adsorption heats close to that of liquefaction of vapor water,⁵ at temperatures close to 273 K. Their specific surfaces, the shape, and dimensions of the pores are determined graphically while adsorbing nitrogen on the polymer at low temperature.^{5–7}

Various polymers and proteins were studied^{8–10} with respect to vapor water at a temperature of 25°C. The polymers that present a mode of connection consisted of the ester groups, which have a weak affinity with respect to the vapor water. On the other hand, the carboxyl groups present a strong affinity with

respect to the adsorbed water. Several synthesized linear polymer reactions at 25°C^{11–13} can be interpreted by using several adsorptions models.

EXPERIMENTAL

Equipment

The adsorption equilibrium of the water vapor by polymer is given with the Mac-Bain thermo balance, especially designed to determine the mass variation of the reaction under controlled conditions of temperature and pressure. The sample is placed in the nacelle and then heated at a temperature of 343 K for 24 h under a dynamic vacuum of 10–6 bar (to obtain a dry and degassed product). To determine the adsorption heats of vapor water on polymer according to the quantity of water vapor adsorbed, we have used a calorimeter SETARAM C 80 coupled with volumetric equipment.

Sample

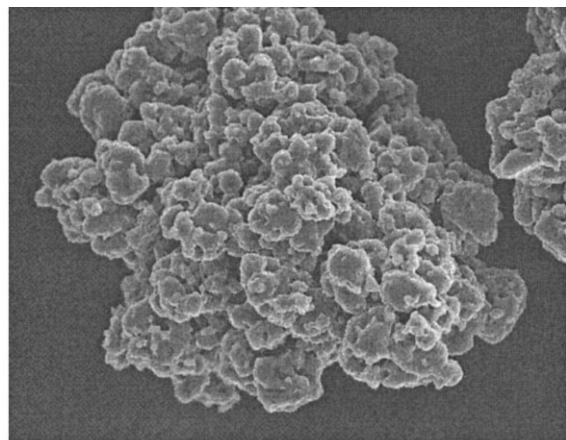
The studied product is a super absorbent product prepared starting from acrylic acid. It is able to absorb 1000 times its weight of water. Indeed, in the presence of liquid water, the polymer inflates instantaneously and quickly to give rise to a soft and transparent gel.^{14,15}

The general aspect of the polymer is presented in the form of deformed spheres [Fig. 1(a)]. The surface aspect appears nonporous [Fig. 1(b)].

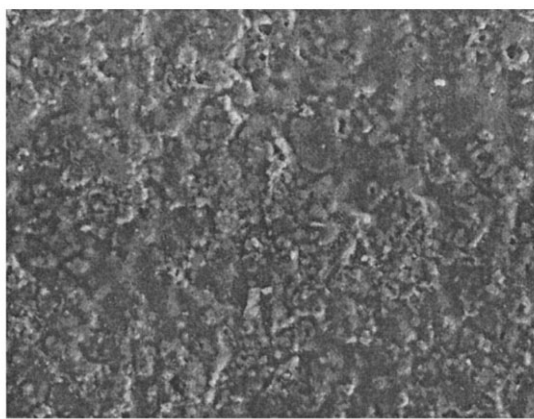
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(a)



(b)

Figure 1 The general aspect of the polymer presented in the form of deformed spheres.

The chemical analysis of polymer by energy disperse spectrometry (EDX) with a micro sounder X (OXFOR) showed that the product contains carbon, oxygen, and sodium. The results obtained with X-ray diffraction showed that the polymer is amorphous. This was also observed with the polymer X5.^{7,16} The polymer consisted of macromolecular chains joined by covalent bonds, and each chain contains a significant number of acid functions. In aqueous medium, these acid functions dissociate and give rise to sites charged (COO⁻). The electrostatic repulsion and elasticity of the polymeric chains involve an expansion of the polymeric network and consequently a swelling of polymer to form the gel.

RESULTS

Specific surface

The study carried out previously on a super absorbent polymer X5 enabled us to conclude that this type of

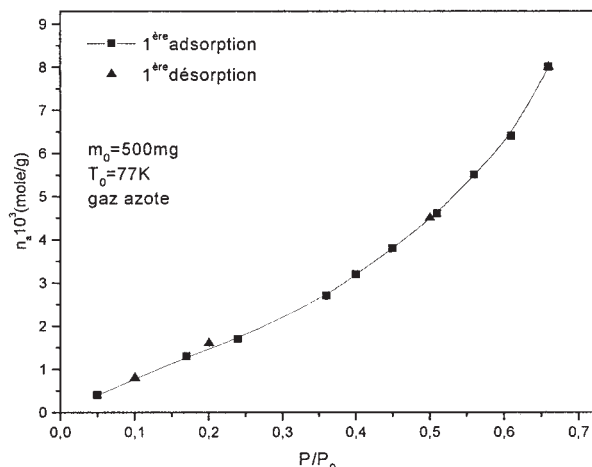


Figure 2 Curve of adsorption and desorption of the nitrogen.

polymers have weak surfaces (lower than 10 m²/g) and are nonporous⁷. The B.E.T. method does not allow evaluating surfaces of these organic polymers with precision. For these systems, the formation of multilayer is done on a part of the surface of the solid, whereas the full-course remains still incomplete. The specific surface of this type of solid can be evaluated with “α_s-plot” method. Figure 2 represents the adsorption isotherm of nitrogen on polymer. It presents the same form as that characterizing the selected reference product (silica gel). The transformation α_s-plot, (Fig. 3) which represents the variation of the moles number of adsorbed nitrogen on polymer according to ace, is a line that passes through origin. The X10 polymer differs from reference product only by specific surface and not by porosity. The specific surface of polymer is then given, starting from the slope of the right-hand side; it is equal to 2.1 m²/g.

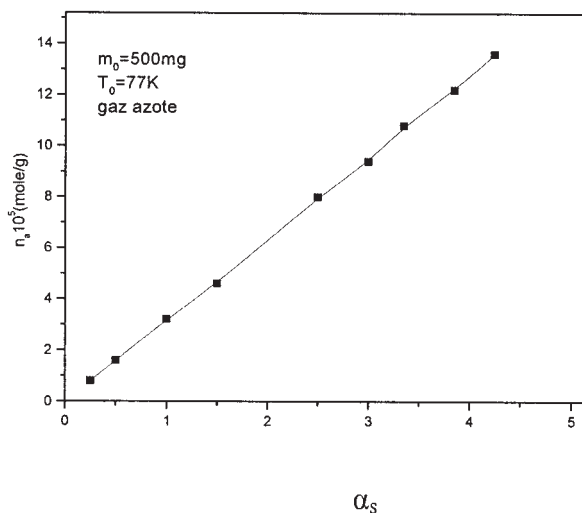


Figure 3 Transform “α_s-plot.”

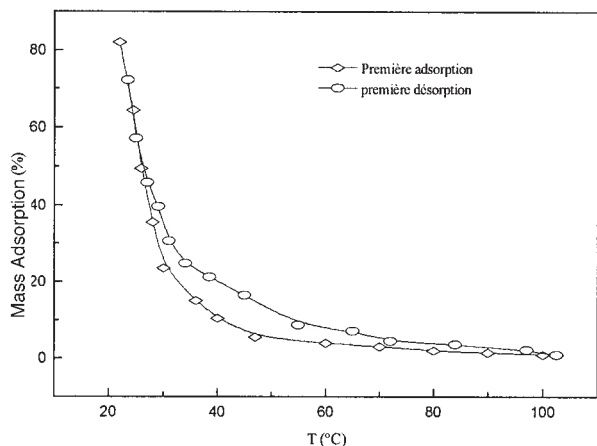


Figure 4 Isobars of adsorption-desorption of water vapor on polymer at $P = 19.8$ mbar.

Adsorption isobars

Two isobars of the first adsorption and following desorption were represented in Figure 4. The adsorption isobar is of type III, according to classification IUPAC.^{17,18} It presents a hysteresis of the H3 type, which is often more or less important according to the nature of the exchangeable ions. The quantity of adsorbed water believes indefinitely in the vicinity of saturation. The adsorption curve does not present stages between its two ends. Figure 5 shows the curves that translate the effect of repeated reactions on the adsorption and desorption reactions.

Adsorption isotherms

The adsorption isotherm of vapor water on macromolecules at $T = 25^\circ\text{C}$ is also of type III (Fig. 6). It is

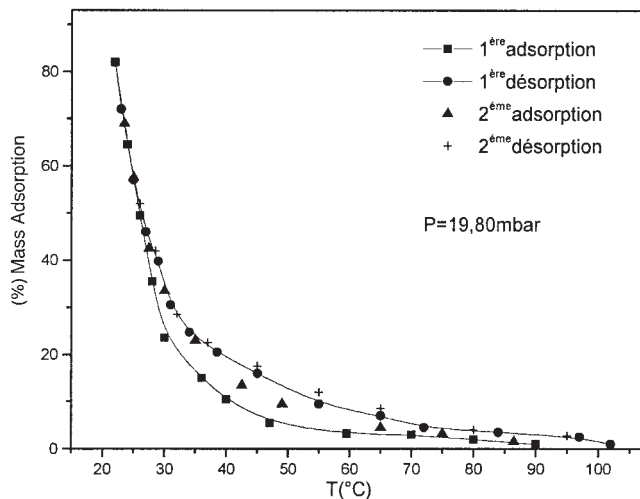


Figure 5 Effect of the repeated reactions on the adsorption and desorption reactions.

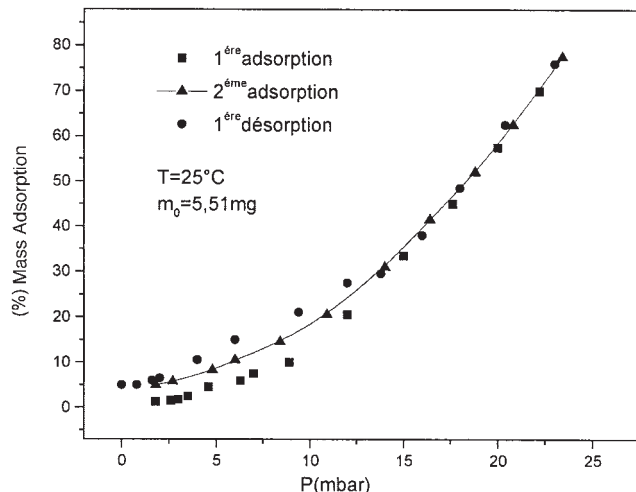


Figure 6 Isotherm of adsorption of water vapor on polymer at $T = 25^\circ\text{C}$.

characterized by a hysteresis, which is not closed again after the initial adsorption reaction. On the other hand, after the second adsorption reaction, the hysteresis is closed again. The activation curve of macromolecules at 90°C (Fig. 7) shows that for temperatures higher or equal to 90°C , the percentage of water eliminated is equal to 14%. This eliminated water corresponds in fact to the water quantity present in the product, including the reticulation water. The water quantity eliminated decreases as the activation temperature of the product decreases to reach a minimal quantity equal to 9% (starting from the temperatures lower or equal to 30°C). This remaining water quantity that corresponds only to reticulation water (strongly dependent) cannot be eliminated at low temperatures.

We have studied the adsorption reactions of water vapor on polymer at low temperatures lower than ambient (5 and 15°C). The adsorption isotherm obtained with $T = 5^\circ\text{C}$ for the initial adsorption reaction

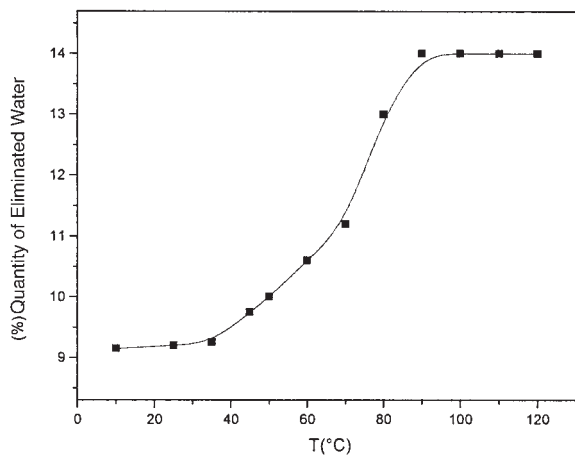


Figure 7 Curve of activation of the polymer X10.

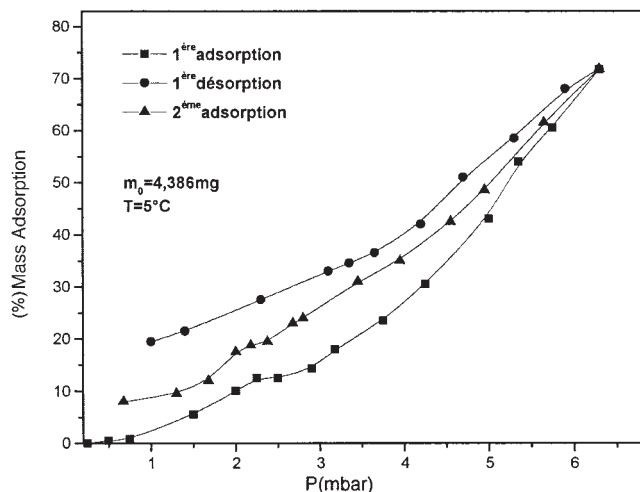


Figure 8 Adsorption-desorption isotherms of water vapor at $T = 5^{\circ}\text{C}$.

and the following desorption isotherm is shown in Figure 8. The adsorption isotherms obtained also have a hysteresis, but with a deformation in the positive direction of type III isotherm. Hysteresis obtained is not closed again after the initial adsorption reaction and the reaction of following desorption. The effect of the repeated reactions adsorption-desorption on the water quantity adsorbed on polymer and consequently on the shape of adsorption curves was examined. We carried out isotherms of adsorption with $T = 15^{\circ}\text{C}$ (Fig. 9), to make sure that the phenomenon of deformation observed with $T = 5^{\circ}\text{C}$ also exists with $T = 15^{\circ}\text{C}$ and to understand the polymer reaction with water vapor at low temperatures.

Calorimetric study

The measurements of the adsorption heat on polymer are carried out by imposing increments of pressure ΔP

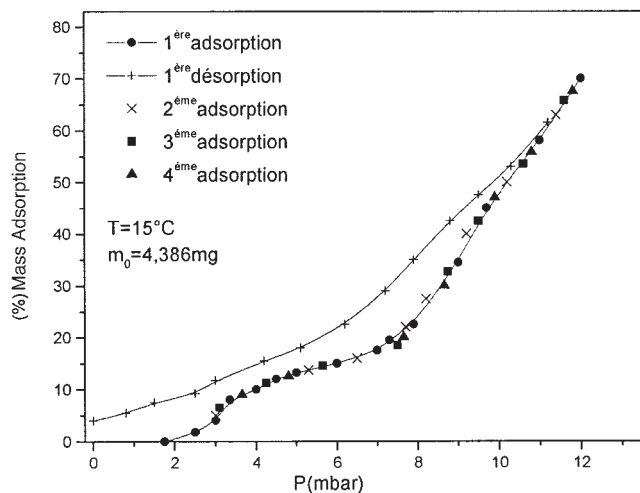


Figure 9 Adsorption isotherms of the water vapor on the polymer X10 at $T = 15^{\circ}\text{C}$.

TABLE I
Heats of Initial Adsorption Reaction of Water Vapor on the Polymer X10 at $T = 25^{\circ}\text{C}$ and $m = 500 \text{ mg}$

Initial adsorbed quantity (%)	Final adsorbed quantity (%)	Heats of adsorption (kJ/mol of water)
0.00	0.40	90.99
0.40	0.78	91.72
0.78	0.90	88.53
0.90	0.98	87.26
0.98	1.25	89.50
1.25	1.75	86.88
1.75	2.15	85.62
2.15	2.60	85.02
2.60	3.05	82.56
3.05	3.40	80.55
3.40	4.26	78.99
4.26	5.10	76.83
5.10	5.85	72.44
5.85	6.70	70.81
6.70	7.50	67.82
7.50	9.12	68.32
9.12	12.5	66.69
12.5	15.00	66.95
15.00	18.50	67.31
18.50	23.20	68.50
23.20	29.50	67.65
29.50	36.50	67.45
36.50	43.20	66.38
43.20	48.50	65.86
48.50	53.25	62.66
53.25	57.30	59.22
57.30	62.51	58.12
62.51	68.96	57.69
68.96	77.60	52.54
77.60	85.50	49.20
85.50	92.02	45.23
92.02	98.65	44.98

lower than 15 mbar on a product temperature (25°C). The values of the adsorption heat obtained according to the adsorbed quantity are given in Table I.

Discussion and conclusion

The adsorption isobars of the nitrogen (Fig. 2) and of the steam (Fig. 4) represent an adsorption process characterized by a multilayer adsorption that occurs before the full-course is complete. For the adsorption reaction of the steam, the multilayer is followed after, by a phenomenon of condensation of the steam on and between the macromolecular chains, which discard the ones of the others during adsorption.^{7,13,19} The quantity of adsorbed water on polymer can reach 80% for a variation in temperature between the cold point and polymer at 5°C . On the other hand, for the same variation in temperature and with the same conditions of product temperature and steam pressure, the polymer X5 can adsorb only 45% of the steam.^{16,20} This result is awaited since the polymer X10 presents an ionization level higher than that of the polymer X5; the

polymer X10 absorbs up to 1000 times its liquid water weight, instead of 500^{14,15} times for the polymer X5.

The shape of the curves can be explained by the fact that, in the first adsorption, the polymer undergoes a deformation or a rearrangement of the polymeric network, which results from a cooperative diffusion due to insertion of the water molecules between the chains followed simultaneously by an expansion of the macromolecular network. The desorption of the water molecules also induces a phenomenon of rearrangement of the polymeric network (cooperative phenomenon of diffusion), which results from the diffusion of the water molecules followed by a tightening of the macromolecular chains.

The fact that the adsorption isobar is closed only toward the high temperatures (higher than 80°C) probably implies that the macromolecular chains remain sufficiently isolated at the end of desorption compared to activated polymer. Consequently, the polymeric chains find neither their forms nor their initial positions. The polymer retains a small quantity of residual water, related to the most active sites of the macromolecule, which prevent the chains from being completely closed again. When the temperature of polymer becomes higher than 80°C, the residual water molecules, which ensure an additional reticulation of the chains, are then eliminated and the hysteresis is closed.

The hysteresis corresponding to adsorption isotherm obtained with $T = 25^\circ\text{C}$ (Fig. 6) is not closed again after the first adsorption and following desorption. On the other hand, it is closed again after the second adsorption reaction. This result can be explained by the fact that, when the polymer is activated (vacuum at a temperature of 90°C), all the water quantity present in polymer is eliminated. With the first adsorption, the polymer adsorbs steam necessary to reach its balance of adsorption. During the following desorption when product temperature is lower than 90°C, the water quantity adsorbed is not eliminated (Fig. 7). Indeed, there remain residual molecules of water strongly related to the most active sites of the macromolecule and in more surrounded by the tightened chains. For this same reason, the curve of the first adsorption cycle does not coincide with the following curves of adsorption and desorption (which coincide between them) before the water adsorbed quantities higher or equal to 50%. For the adsorption isobar (Fig. 4), the hysteresis is closed; but, at high temperatures (higher than 80°C) all residual molecules is eliminated. The adsorption isotherms should also present hysteresis that are closed, but at product temperatures higher than 80°C.

We can conclude that three types of water molecules exists related to polymer:

- Strongly dependent water, which can be eliminated at temperatures higher or equal to 90°C, allot to residual water which ensures an additional reticulation of the macromolecular chains.
- Adsorbed water on polymer, dependent on the sites charged with the macromolecule, when the quantity adsorbed lies between 5 and 50% (Fig. 6).
- Slightly water bound, when the water percentage adsorbed is higher than 50%, which corresponds to related water to the macromolecule by weak connections (ion-dipole) and also trapped between the polymeric chains.
- difference in swerve between the curve of adsorption and that of following desorption at the same temperature (Figs. 6, 8, and 9) vary with the temperature imposed on polymer. Indeed, more the adsorption temperature decreases more the difference between the two curves grows. This difference can be probably due to the effect of chains, which become increasingly reticules as the temperature of the sample decreases, during adsorption and desorption reactions. Indeed, when the reaction is carried out at a temperature of polymer lower than ambient, the water molecules retained or trapped by the macromolecular chains are not easily released during desorption. This can be explained by the fact that the polymeric chains present in more than normal reticulation (i.e., an additional reticulation) that prevents the water molecules from being desorbed. This additional reticulation of the chains is favored in the field of the low temperatures. We can note for example that with $T = 15^\circ\text{C}$ and vacuum, the final adsorption rate of polymer after the first desorption is equal to 4%; on the other hand, when the reaction temperature is equal to 5°C, it is only 6%. When the reaction temperature increases, under the effect of the temperature, this additional reticulation is reduced and the adsorption curves and those of following desorptions approach the others. The relative curves of the first adsorption and that of following desorption at the same reaction temperature will have to coincide at higher temperatures or equalizes with 90°C. This effect of chain, which is a consequence of the effect of temperature (shown in Fig. 4) is confirmed by the following points:
- For the adsorption rates lower than 20, there is a difference between the curves of adsorption and those of following desorption, which can be allotted for chain purpose. This difference is important in the case of the low temperatures and is reduced as the reaction temperature increases to become equal to 0. The two curves coincide when the sample temperature becomes higher or equal to 90°C.

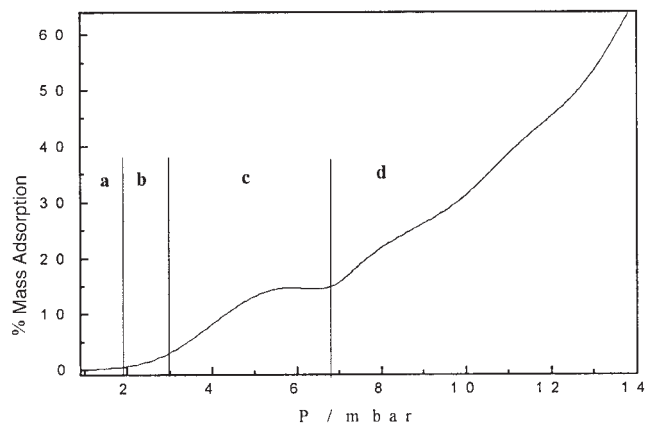


Figure 10 Adsorption isotherms of water vapor on the polymer X10 at lower temperature.

- For adsorption rates ranging between 20 and 50, the polymeric chains are sufficiently isolated from the others, and the chain effect becomes secondary.
- At adsorption rates higher than 50, one obtains a saturation phenomenon of the chains followed by a condensation phenomenon of water vapor on the macromolecules.
- adsorption isotherms obtained with $T = 5^{\circ}\text{C}$ and $T = 15^{\circ}\text{C}$ can be represented as Figure 10. We can distinguish four adsorption fields: The first field (a) corresponds to adsorption of the first molecules of water on the macromolecular chains without leading to chain separation. Indeed, the first molecules will be adsorbed on the most active and easily accessible sites (localized on the surface of the macromolecules).
- After the first adsorption of water molecules (field (b)), the following molecules likely to be adsorbed will have to draw aside the macromolecular chains to reach the active sites located between the macromolecular chains. The adsorption phenomenon during this stage will require more energy, compared with that during the first stage and is less favored because of the constraints that result from chain separation.
- In the third adsorption field (c), the macromolecular chains begin to discard from the others. Consequently, the polymeric network undergoes a deformation, which results in the spacing out of the macromolecules from each others inducing a swelling of the polymer. The adsorption phenomenon during this third stage is more favorable, compared with that during the second stage. The adsorbed quantity then undergoes a fast increase and the adsorption curve deviate from type III isotherm. Indeed, in more of the adsorption process, there is a phenomenon of deformation due to a rearrangement of the polymeric network, and

consequently, the adsorption isotherms obtained present a deformation in the positive direction than type III isotherm.

- During last stage (field (d), the water adsorbed percentages are higher than 16%), the macromolecular chains are drawn aside and continue to deviate from the others, and the interactions between adsorbing and adsorbate are relatively weak. It is a succession of the formation of the monolayer followed by a multilayer and in consequence of a condensation phenomenon of the steam enters and on the macromolecular chains. The form of the adsorption isotherms coincide with that of type III.
- Figure 11 shows the evolution of the heat of the initial adsorption reaction of water vapor on the polymer, according to the equilibrium water quantity adsorbed. The figure can be divided into three fields:
- The first relative to steam adsorbed quantities lower than 7% corresponds to important heats of adsorption reaction. In this field, the value of the adsorption heat decreases with the adsorbed water quantity. As previously described, it is the adsorption of water that is strongly related to the most active sites of the macromolecule and which ensures in more the additional reticulation of the macromolecular chains. This water can be eliminated only starting from the temperatures higher than 80°C under vacuum atmosphere (Fig. 7).
- In the second field, corresponding to steam adsorbed quantities on polymer ranging between 7 and 50%, the heat of adsorption reaction remains constant when the quantity of matter adsorbed on polymer increases. This field can be allotted to the adsorption of the steam on the charged sites of

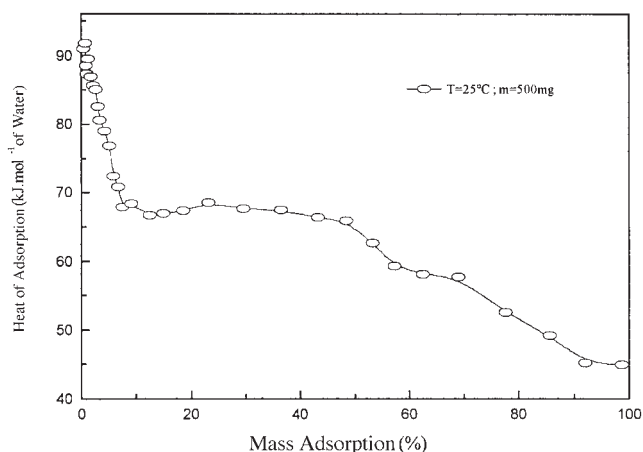


Figure 11 Adsorption heat of the vapor on the polymer X10. The measurements are taken at the time of the first adsorption.

macromolecules; they are in fact a field steam pressures and temperatures where the formation of the monolayer is followed by the multilayer, which starts its formation before the monolayer is complete.^{13,17-19}

- In the last field, for adsorbed quantities higher than 50%, the heat of reaction decreases to reach a value of 44 kJ/mol. Indeed, we have a phenomenon of water vapor condensation on and between the macromolecular chains, and the heat of reaction becomes identical to that of liquefaction of water vapor. The water molecules slightly related to the macromolecule by connections ions-dipoles are indeed only trapped by the macromolecular chains.
- The recent results show that the polymer X10 have very interesting characteristics and a very broad of application field. In the field of renewable energies, a material that has a heat of adsorption reaction high, that reaches 91 kJ/mol for the first water molecules adsorbed with a adsorbed quantity of matter, and that can reach 80%, is to be retained insofar, as it will present fast kinetics of reaction with a good behavior at cycling (conser-

vation of the properties after several cycles adsorption-desorption).

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