

# Swelling of Superabsorbents Polymers in an Aqueous Medium

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**ABSTRACT:** The polymers studied are superabsorbents materials. They were synthesized by inverse suspension polymerisation of acrylic acid. The polymers studied, X10 and X5, are different in their degree of ionisation. In fact, our objective was to increase the amount of water that may be stored by the polymer. In this article, we investigated not only the effect of temperature and pH on the saturated water absorbency of polymers X10 and X5, but also various swelling behaviours of polymer X10 in different saline solutions. The results show that for temperature ranging from 10 to 90°C, the effect of temperature on the saturated water absorbency is rather limited when the

superabsorbent is swelled by distilled water. Further, water absorbency of X10 and X5 is strongly affected by the pH value. The results also indicate that saline solutions can weaken the swelling abilities of the polymer X10. Water absorbency of polymer X10 in aqueous chloride salt solutions has the following order:  $\text{Na}^+ = \text{K}^+ = \text{NH}_4^+ > \text{Ca}^{2+} = \text{Mg}^{2+}$  all through the range of investigated concentration. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2479–2484, 2010

**Key words:** polymers; superabsorbant; water absorbency; swelling

## INTRODUCTION

Superabsorbents are slight crosslinked hydrophilic polymers that can absorb, swell, and retain thousand times of aqueous liquids, namely water of their weights. Therefore, superabsorbents have great advantages over traditional water absorbing materials. Because of their excellent characteristics, superabsorbents are widely used in many fields such as agriculture and horticulture.<sup>1,2</sup> In such applications, water absorbency, and water retention are essential. Most of these kinds of polymers are commonly synthesized on the basis of acrylic monomers, such as neutralized acrylic acid, acrylamide, and the salt of the acid, by solution polymerization,<sup>3</sup> or inverse suspension polymerization.<sup>4</sup> Therefore, foamed polymerization has been found to be an alternative method for preparing superabsorbent polymers with enhanced absorption rate.<sup>5</sup>

The water absorbency of polyacrylates superabsorbents in distilled water depends on the reaction conditions such as the initiator content, initial monomer concentration, and crosslinker content.<sup>6</sup> However, the swelling behaviour of polyacrylate in the mixture of water and hydrophilic solvent including methanol, ethanol, ethylene, glycerol, acetone, dimethyl formamide, and dimethyl sulfoxide depends

on the mixture concentration by changing the solubility parameter of the solvent-water mixture.<sup>7</sup> Recently, the preparation of polymers by introducing clays such as attapulgite,<sup>2,8–12</sup> montmorillonite,<sup>13</sup> and kaoline<sup>14</sup> has attracted attention because of their relative low cost and high water absorbency. Another advantage of its systems is the possibility of biodegradation.

Extensive attention has been directed toward superabsorbents polymers prepared through graft copolymerization of vinyl monomers onto the chain of natural polymers such as starch,<sup>15,16</sup> cassava starch,<sup>17,18</sup> carrageenan,<sup>19</sup> and chitosan.<sup>20</sup> Incorporation of these systems into other synthetic polymers not only reduces our dependence on petrochemical-derived monomers but also provides materials in which the biopolymer portion can biodegrade rapidly in the environment. In this article, we compare the swelling behaviour of two acrylic-based superabsorbent polymers X10 and X5. They are synthesized by inverse suspension polymerization of acrylic acid using *N,N'*-methylenebisacrylamide as crosslinker. Indeed, the polymer X10 is more ionic than the polymer X5 with more acid functions able to be ionized in aqueous medium.

## EXPERIMENTAL PROCEDURES

### Sample

The studied materials are superabsorbents polymers (X10 and X5) marketed under the reference:

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NORSOLOR C.A.S. 9033-79-8. They are based on acrylic acid, synthesized through inverse suspension polymerization by using *N,N'*-methylenebisacrylamide as a crosslinker. The polymer X10 is presented in the form of small deformed spherical balls, which was not the case of the X5 polymer. The grain's diameter varies between 10 and 100  $\mu\text{m}$ . The major functional grouping constituting the X10 polymer was identified by IR spectroscopy.<sup>21</sup> Its morphological aspect appears nonporous and presents a weak specific surface.<sup>21</sup>

### Measurement of water absorbency

A weighted quantity of dry sample (10 mg) was introduced in a tube. The distilled water or saline solution was gradually added to the polymer until absorption equilibrium was reached. The fully swollen hydrogel was separated from the unabsorbed water by using filter paper. Then, the hydrogel was weighted. Relative water absorbency was calculated by using the following equation:

$$Q_{\text{H}_2\text{O}} = \frac{m_2 - m_1}{m_1}$$

where  $m_1$  and  $m_2$  are the weights of the dry sample and the swollen sample, respectively.

The  $Q_{\text{H}_2\text{O}}$  value was calculated as grams of water per grams of sample.

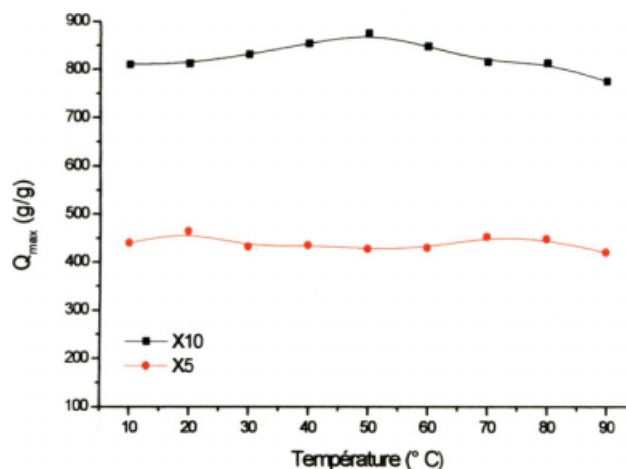
### Measurement of pH's gel

The preparation method of gel is similar to that followed in the measurement of the water absorption. The desired basic or acidic pHs of absorbed solutions were adjusted by adding NaOH or HCl solutions. The measurement of pH's gel is made by a pH metre of type pH 209-209R Bench-top with an included electrode HI 1332B (accuracy  $\pm 0.01$ ). To calibrate the pH metre electrode, we have used a buffer solution with known pH. A solution with pH = 7 and pH = 2 for acidic pH of absorbed solutions. For basic absorbed solutions, a solutions with pH = 7 and pH = 10 were used. Before each measurement, the pH metre cell is rinsed by distilled water. It was then immersed in the hydrogel. The pH of the gel corresponds to the pH of the cell when the medium's equilibrium was reached.

## RESULTS AND DISCUSSION

### The effect of temperature on water absorbency

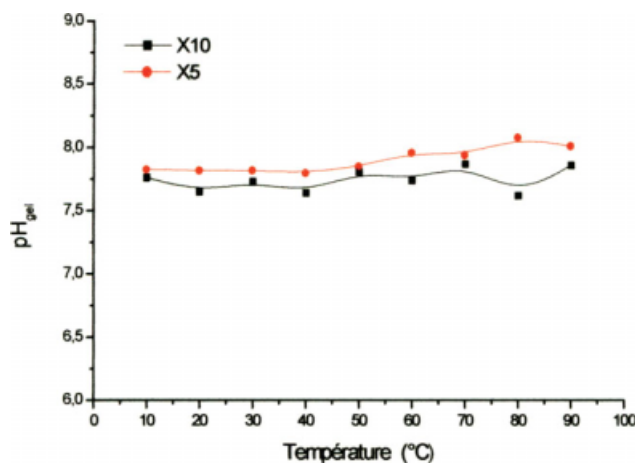
The effect of the temperature on the water absorbency of the superabsorbents X10 and X5 in distilled water was investigated and results are shown in Figure 1. The water absorbency of the superabsorb-



**Figure 1** Effect of temperature of distilled water on absorbency of X10 and X5. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ent X10 increased as the temperature increased from 10 to 50°C. This result can be due on the one side, to the purely chemical effect which should promote the intensity of repulsive forces between charged sites ( $\text{CO}_2^-$ ) by moving the acid-base equilibrium to ionic form of acid, and on the other side to the increase the flexibility of macromolecular chains, given that the swelling equilibrium is a result of compensation between the repulsive forces and the elasticity of the polymer chains.<sup>22,23</sup> However, when the temperature value ranged from 50 to 90°C, the water absorbency decreased slightly. This event may also be explained by increasing both the ability to the deformation of macromolecular chains and water activity (thermal agitation) as the temperature increased. Thus, the ability of polymer chains to trap water molecules is reduced, and, therefore, the water absorbency decreases. The observation of the curve corresponding to polymer X5 (Fig. 1) shows that the effect of temperature on the absorption capacity of the polymer is almost negligible. This result is expected, given that this polymer is characterized by a degree of ionization less than that of polymer X10. Indeed, the number of acid functions that may be ionized in the case of polymer X5 is lower, and, as a result, the absorption capacity is reduced by half.

The change of the gel's pH, as a function of temperature, was also studied. Figure 2 shows this change. The curve on X10 is placed below the one that corresponds to polymer X5. In addition, polymers X10 and X5 have ionization degrees of about 60 and 50%, respectively. The analysis shows that the effect of temperature on the acid-base balance hence the water absorbency remains low. In fact, the number of ionized functions is weakly affected by the temperature.

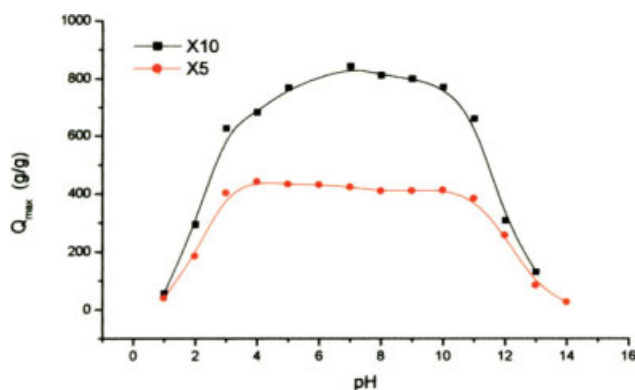


**Figure 2** Evolution of gel's pH as function of temperature in distilled water. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

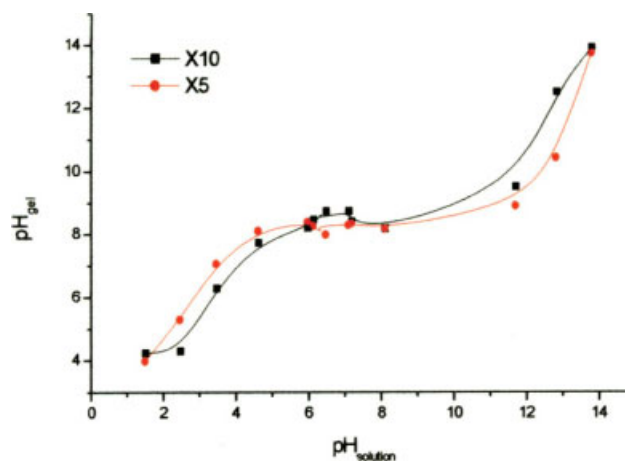
### Effect of pH on the water absorbency

The effect of pH on the swelling behaviour of the polymers X10 and X5 was also investigated. Figure 3 shows the swelling properties of the polymers at different pH values. The pH values of the external solution were adjusted through the addition of HCl and NaOH solutions in water.

The absorbency of the superabsorbents X10 and X5 increased sharply as the pH value increased from 1 to 5. This behaviour may be explained by buffer action of the carboxylates groups with an acid or base. In an aqueous solution at low pH, the carboxylates groups on the polymeric chains can turn into carboxylic acid groups. The carboxylic acid groups show, neutral electric charge and lead to a reduction of the repulsion between groups on the polymeric chain. Therefore, the electrostatic repulsion of the polymer's chains decreases and this leads to a reduction of the water absorbency. At high pH values (11–14), the water absorbency decreases drastically.



**Figure 3** Effect of pH on the water absorbency of X10 and X5. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



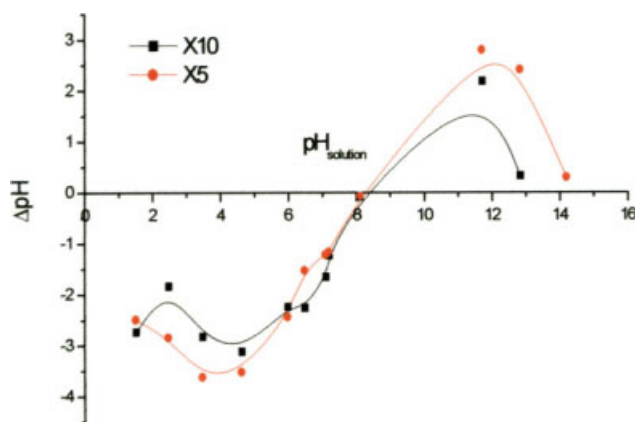
**Figure 4** pH of gels X10 and X5 according to pH of external solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Indeed, the carboxylic acid groups on the polymeric chains can turn into sodium carboxylates groups. Consequently, the screening effect of the counterion ( $\text{Na}^+$ ) on the polyanions chains leads to a reduction in the expansion of the network. In addition, the change in the water absorbency was slight, from  $\text{pH} = 6$  to 11. Indeed, in this area of pH, there is a compensation in electrostatic repulsions between charged sites ( $\text{CO}_2^-$ ) and the screening effect due to counterion. Figure 3 indicates that basic environment has a greater impact on water absorbency than that of acidic environment. Indeed, in a basic environment for pH values greater or equal to 12, the absorption never gets close to zero. This result can be explained by the main cation–cation repulsive forces, which leads to the expansion of the polymeric chains to retain water between them.

To better visualize the effect of pH environment on the behaviour of polymer, the evolution of gel's pH according to the pH of external solution was investigated. Figure 4 shows this evolution.

The analysis of curves shows that, under acidic environment, the pH of gel is higher than that of the pH of the absorbed solution. The swelling behaviour of the polymer results in a growth of the medium's pH, making the middle less acid. In a basic medium, the difference between the pH of the gel and the absorbed solution is less pronounced. For pH values close to 8, both pH values are quite similar. This difference may be due to a difference in degree of ionization of X10 that is superior to that of X5.

To highlight this result, we represent, in Figure 5, the variation of  $\Delta\text{pH}$  ( $\Delta\text{pH}$  corresponds to the pH of the gel subtracted from the pH of external solution) according to the pH of the absorbed solution by the polymer. Observation of Figure 5 shows that this difference is negative for the pH of the solution lower than 8.4. Beyond this value, the  $\Delta\text{pH}$  becomes



**Figure 5** Variation of  $\Delta\text{pH}$  depending on the pH of absorbed solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

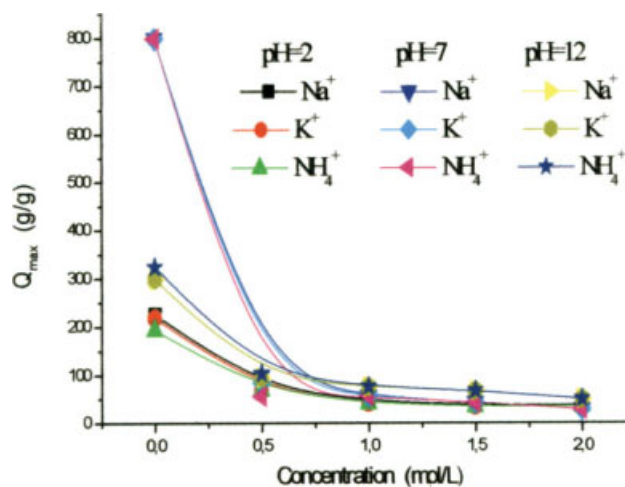
positive. In acidic environment,  $\Delta\text{pH}$  reaches a value equal to 4, and in basic pH, this difference in pH has a value equal to 2.8.

This result can be explained by the behaviour of the polymer depending on the nature of the environment. In an acidic medium, the negative gap of pH between the two media may be due to the significant amount of hydroniums ions, thus moving physicochemical balance in the direction of protonation of the carboxylate groups. Therefore, the pH of the medium (gel) is higher than that of the absorbed solution. However, in an alkaline medium (pH values higher than 8 and less or equal to 12), carboxylate groups are converted into sodium carboxylate. This may also lead to an increased pH of the medium (gel). Consequently, the pH of the medium (gel) is higher than the one in absorptive solution.

#### Effect of various cations on water absorbency of the polymer X10

It is important to investigate the swelling behaviour of the polymer X10 in various salt solutions to expand their application especially for agriculture and horticulture, and to study the effect of kind and valence of cations on water absorbency of the polymer. Figures 6 and 7 show respectively the effect of various alkali metal ions and alkaline earth metal ions on water absorbency of polymer X10 for three pH values 2, 7, and 12.

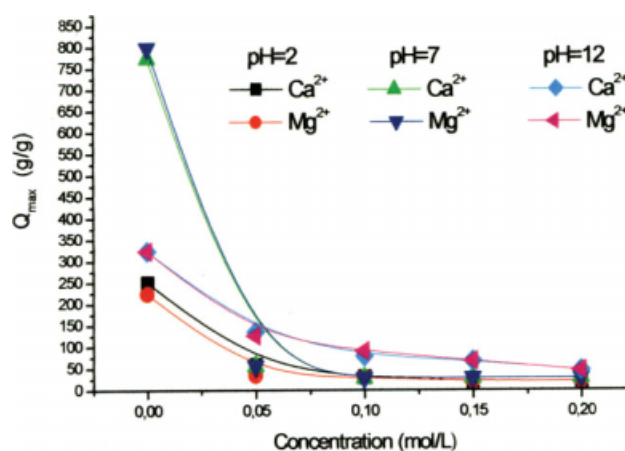
Generally, the water absorbency decreases with the increase of the concentration of various cations. This result is attributed to the fact that the osmotic pressure difference between the polymeric network and the external salt solution concentration increases. In addition, the penetration of counterions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ) into the network allows, on the



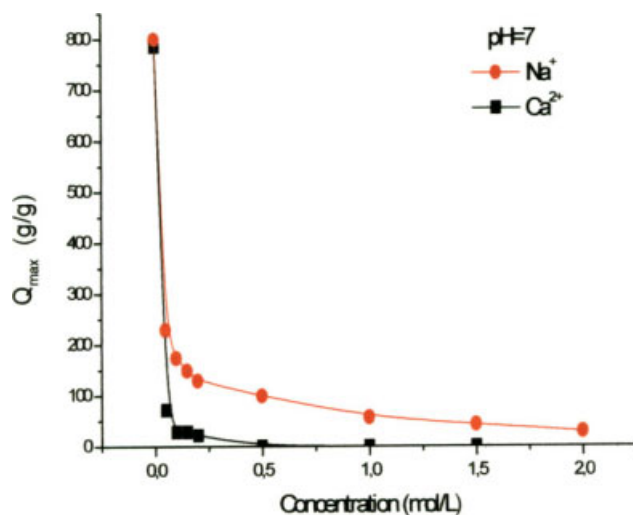
**Figure 6** Water absorbency of polymer X10 in aqueous NaCl, KCl, and  $\text{NH}_4\text{Cl}$  solutions with various ionic strengths. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

one hand, the screening effect of them and on the other hand, it makes easier the migration of the trapped water between the polymer chains to the external environment (free water).

Figure 6 also shows that the monovalent cations  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  have nearly similar effect on the water absorbency  $Q(\text{NaCl}_{(\text{aq})}) = Q(\text{KCl}_{(\text{aq})}) = Q(\text{NH}_4\text{Cl}_{(\text{aq})})$ . This result is in accordance with the result reported by Zhang et al.<sup>12</sup> by studying the effect of a series of monovalent cations on the absorbency of polyacrylamide/attapulgit superabsorbent composite. These authors have noticed that for a given concentration, monovalent cations have the same effect on the water absorbency of the poly(acrylamide/attapulgit) gel, and there is no relationship with radius of cation or the nature of anion.



**Figure 7** Water absorbency of polymer X10 in aqueous  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions with various ionic strengths. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



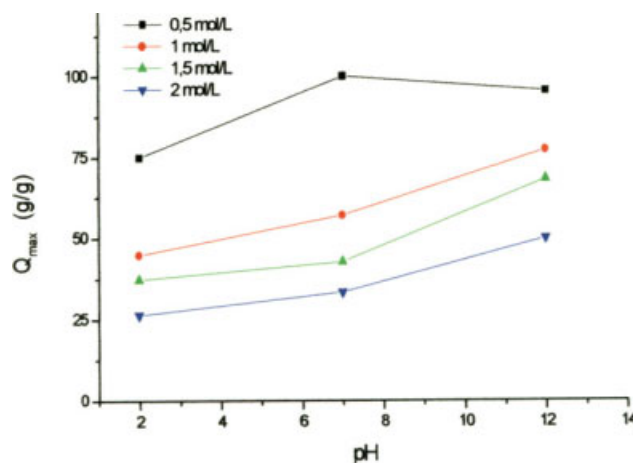
**Figure 8** Water absorbency of polymer X10 on X10 in aqueous NaCl and CaCl<sub>2</sub> solutions with various ionic strengths. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The results described in Figure 7 also showed that the influence of two different alkaline earth metal ions with common anion (Cl<sup>-</sup>) on water absorbency of the polymer X10 is nearly the same all through the range of the investigated concentration  $Q(\text{Mg}^{2+}) = Q(\text{Ca}^{2+})$ .

To compare the effect of cation's valency, we have represented on the same figure (Fig. 8), the change of water absorbency behaviour of polymer X10 in different salt solutions of NaCl and CaCl<sub>2</sub>. It can be seen from Figure 8 that absorbency in NaCl solution is higher than that in CaCl<sub>2</sub> solution. In fact, the effect of divalent cation on water absorbency of polymer X10 is more evident than with a monovalent cation. This result may be explained either by the complex formation ability of the carboxylate groups by divalent cations including intermolecular and intramolecular complexes, or because one multivalent ion is able to neutralize several charges inside the gel. Consequently, the crosslink density of the network increases, whereas water absorption decreases.

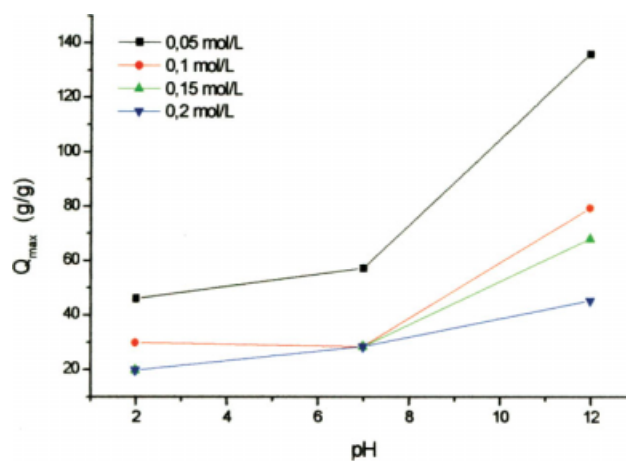
The effect of the cation's concentration of NaCl and CaCl<sub>2</sub> solutions on the absorbency of polymer X10 in relation with the pH environment is represented in Figures 9 and 10, showing water absorbency of polymer X10 depending on the pH of external solution for different concentrations of cations.

The analysis of Figure 9 shows the effect of different concentrations of monovalent cations on the absorbency of polymer X10 depending on the pH. For a given pH value of the solution, as soon as the cation concentration increases, the absorbency decreases, which is in accordance with the results



**Figure 9** Water absorbency of polymer X10 depending on the NaCl solution's pH for various concentrations of cations. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

obtained previously. In fact, at a concentration of 0.5 mol/L, the water absorbency in NaCl solution varies in the following order:  $Q(\text{pH} = 7) > Q(\text{pH} = 12) > Q(\text{pH} = 2)$ . This result is logical according to the study of the effect of pH on the swelling gel (Fig. 3). From a concentration greater or equal to 1 mol/L, the absorbency of polymer X10 in NaCl solutions varies in this order  $Q(\text{pH} = 12) > Q(\text{pH} = 7) > Q(\text{pH} = 2)$ . In fact, for a pH value equal to 12, the number of ionized acids functions exceeds the number of ionized acids functions at pH equal 2 or 7. Also the screen effect is maximum at pH = 12, in fact, at pH = 12, the middle contains the cations studied and those coming from the dissociation of soda. So, the fact that the water absorbency at pH = 12 is higher than the water absorbency at pH = 7 may be acceptable in case that the effect of



**Figure 10** Water absorbency of polymer X10 depending on the CaCl<sub>2</sub> solution's pH for various concentrations of cations. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ionisation is the one phenomenon governing the swelling of the polymer. Indeed, the swelling equilibrium results of compensation between different factors, namely, the forces of electrostatic repulsion between polyanions and the elasticity chains. But in addition to these factors, other electrostatic interactions between cations ( $\text{Na}^+$ ) present in the environment, thus contributing to a further expansion of the network polymer may appear. The importance of these forces depends on many factors such as the gel temperature, the pH of the solution and cation concentration. The swelling behaviour of X10 gel in an environment containing divalent cations (Fig. 10), and for low concentration, shows a similar effect like monovalent cation, especially for concentration greater than 1 mol/L ( $Q(\text{pH} = 12) > Q(\text{pH} = 7) > Q(\text{pH} = 2)$ ). Indeed, in addition to the screening effect, divalent cations present the complex formation ability of the carboxylate groups. However at pH equal to 12, the environment contains cations  $\text{Ca}^{2+}$  and cations coming from the dissociation of soda ( $\text{Na}^+$ ). Therefore, we can explain this result ( $Q(\text{pH} = 12) > Q(\text{pH} = 7)$ ) by the main electrostatic repulsion cation-cation type ( $\text{Ca}^{2+}$ - $\text{Ca}^{2+}$ ), ( $\text{Ca}^{2+}$ - $\text{Na}^+$ ) and ( $\text{Na}^+$ - $\text{Na}^+$ ), thus promoting the expansion of the network polymer at pH = 12. A similar result was obtained with the other cations  $\text{K}^+$ ,  $\text{NH}_4^+$ , and  $\text{Mg}^{2+}$ .

### CONCLUSION

This article is a comparative study of two superabsorbent polymers prepared from acrylic acid and synthesized by an inverse suspension polymerization. The absorption properties of polymer X5 in distilled water and those of polymer X10 in both distilled water and different saline solutions were discussed. The effect of some physical-chemical parameters (temperature, pH, concentration on cations of the external solution) on the water absorbency of polymers has also been studied. Indeed, the impact of the temperature of the external solution on the water absorbency has shown that this temperature has a limited effect on the water absorption of polymers X10 and X5. However, the water absorbency depends heavily on pH values of the solution absorbed. The swelling behaviour of polymer X10 in

a series of cationic solutions has shown that the presence of cations in the absorbed solution leads to the decrease the polymer's water absorbency with the increase of the ionic strength of the external solution. The impact of divalent cations is more accentuated in comparison with that of monovalent cations. This result may be due to the possibility of complexation of carboxylates groups by multivalent cations, which can lead to the formation of intramolecular and intermolecular complexes, and, consequently, to the increase of the crosslink density of polymeric network.

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