CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of The Hydrolyzed Starch-g-Poly(acrylic acid) Copolymer by Infrared Spectrophotometry.

Theoretically, graft copolymerization of vinyl monomer onto starch is always accompanied by homopolymer formation. The grafting products of the present work were thus characterized by an FT-IR technique to detect the presence of the grafted product after the homopolymer was removed.

Infrared spectra of cassava starch, and the hydrolyzed starch-g-poly(acrylic acid) copolymer in the form of KBr pellets are reported in Figures 4.1 - 4.2

The FT-IR-spectrum of cassava starch in Figure 4.1 shows the following important peaks:

Wavenumber, cm^{-1}	Assignment
3,500-2,500	: O-H stretching
2,931	: C-H stretching of CH_2
1,462	: C-H scissor bending of CH_2

Wavenumber, cm^{-1}	Assignment
1,159	: C-O-C stretching
1,084	: C-O stretching
710	: C-H rocking of CH_2

The FT-IR spectrum of the hydrolyzed starch-g-poly (acrylic acid) copolymer in Figure 4.2 shows the following important peaks:

Wavenumber, cm^{-1}	Assignment
3,500-2,500	: O-H stretching
2,930	: C-H stretching of CH_2
1,709	: C=O stretching
1,566	: C=O and C-O asym. stretching of the carboxylate anion
1,460	: C-H scissor bending
1,408	: C=O and C-O sym. stretching of the carboxylate anion
1,157	: C-O-C stretching

The FT-IR spectrum of Cassava starch in Figure 4.1 gives absorption bands at 3,400 and 1,000-1,100 cm^{-1}, the characteristics of amylose containing in the starch. Obviously, several distinguished peaks observed in the FT-IR spectrum of hydrolyzed starch-g-poly(acrylic acid) copolymer in Figure 4.2 indicate the occurence of the graft copolymerization of acrylic acid onto starch in which the

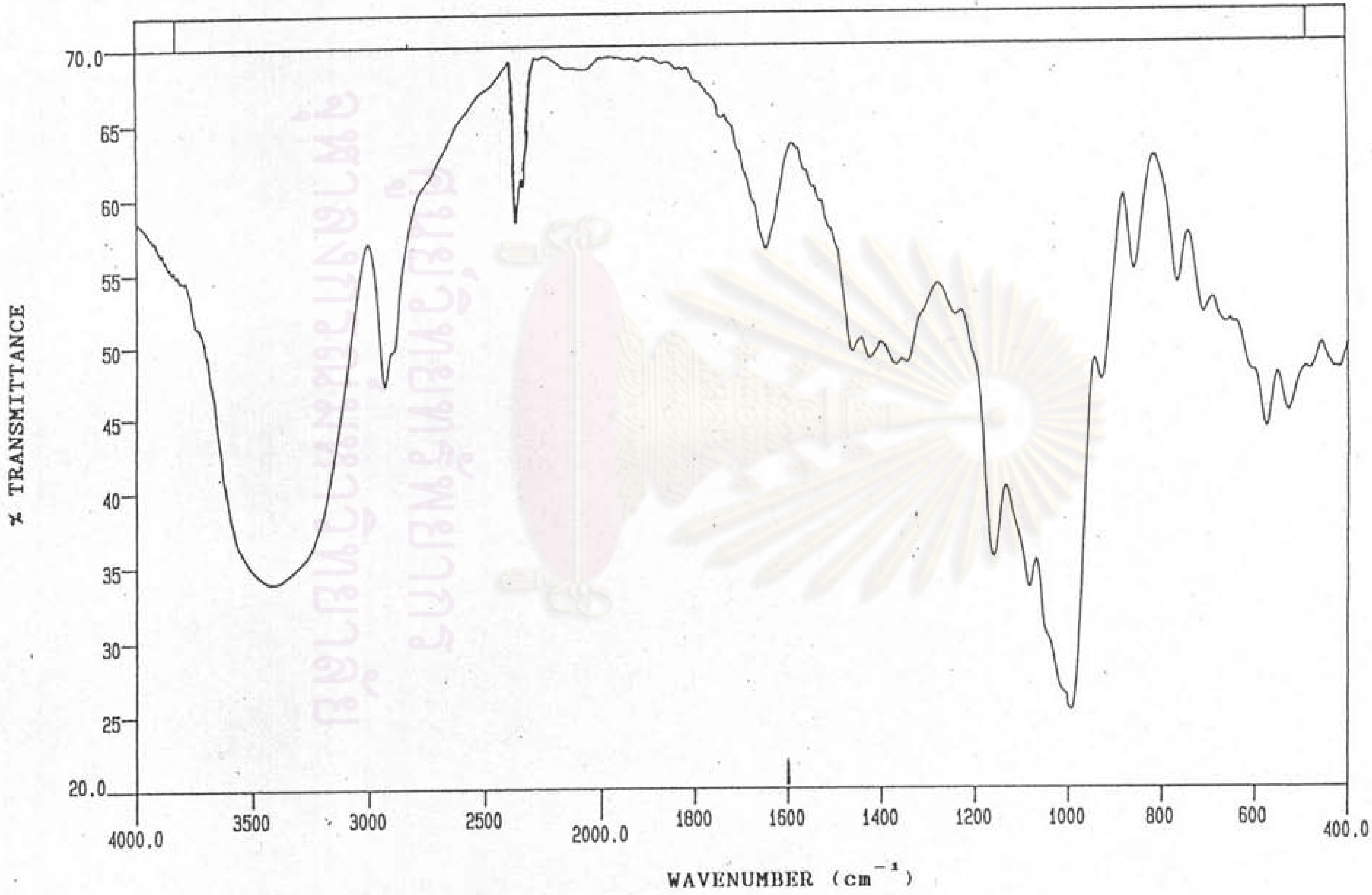

Figure 4.1 Infrared spectrum of the dried cassava starch

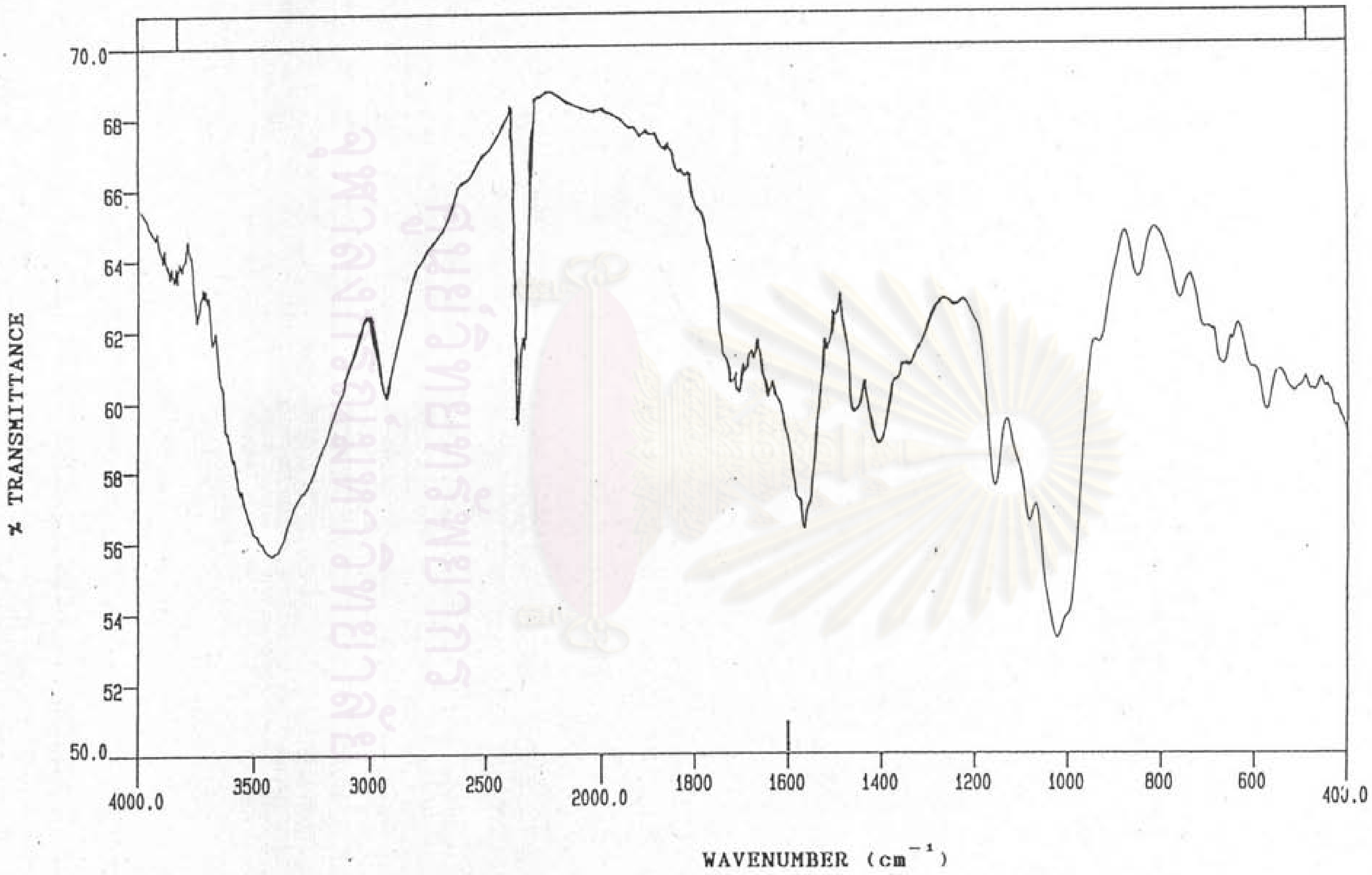

Figure 4.2 Infrared spectrum of the hydrolyzed starch-g-poly(acrylic acid) copolymer

absorption peaks of the C=O stretching occur at 1709 cm^{-1} and the C=O and C-O asymmetry and symmetry stretchings of carboxylate anions occur at 1566 and 1408 cm^{-1} (79), respectively. The latter two peaks indicate that poly (acrylic acid) grafts are converted into their inorganic salt (potassium polyacrylate) when the copolymer is saponified.

4.2 The Grafted Polymer Molecular Weight.

In this work, there is a problem of separating the poly(acrylic acid) graft chains from the polysaccharide backbone by the acid or enzyme hydrolysis methods (such as α-amylase to break (1->4-α-D linkage), and followed by a precipitation method with the nonsolvent of poly(acrylic acid) such as hexane, toluene, carbon tetrachloride. By this method, there is no precipitate from the precipitation. Thus, it is essential to determine the average molecular weights of the poly(acrylic acid) graft chains by GPC.

The retention times determined by GPC of poly-(ethylene oxide) standards (TSK SE-2, SE-4 and SE-5, with molecular weights 24,000, 46,000 and 85,000) are 91.72, 86.17 and 80.93 minutes, respectively. It is found that the relationship between log (molecular weight, M) and the retention time is linear (as shown in Figure 4.3). This result correlates quite well with the calibration curve of log (M) versus elution volume (V_e) or retention time (t_R) (80). Curve fitting procedures permit the determination of the moleculear weight at any retention time within the range covered. This relationship gave essentially an linear calibration curve such that the following equation could be expressed.

$$\log (M) = A - Bt_R \tag{4.1}$$

where

M = molecular weight

t_R = retention time

A and B = constants

The saponified starch-g-poly(acrylic acid) copolymer by acid hydrolysis gave broken, linkages of polysaccharide (1->4-α-D) and (1->6-α-D), to small molecules such as mono-, di-saccharide before this solution was injected to the GPC.

The GPC chromatographs obtained from Baseline-810 software of the saponified starch-g-poly(acrylic acid) copolymers are similar which are shown in Figure 4.4. There are two peaks inseparable although the flow rates of the mobile phase were changed from 0.5 to 0.1 cm^3/min. The peaks data are in Appendixes B.1-B.3. This result shows that acid, hydrolyzes polysaccharide, perhaps to the oligomer of starch (not to mono-, and di-saccharide). The size of the oligomer of starch is close to the grafted poly(acry-

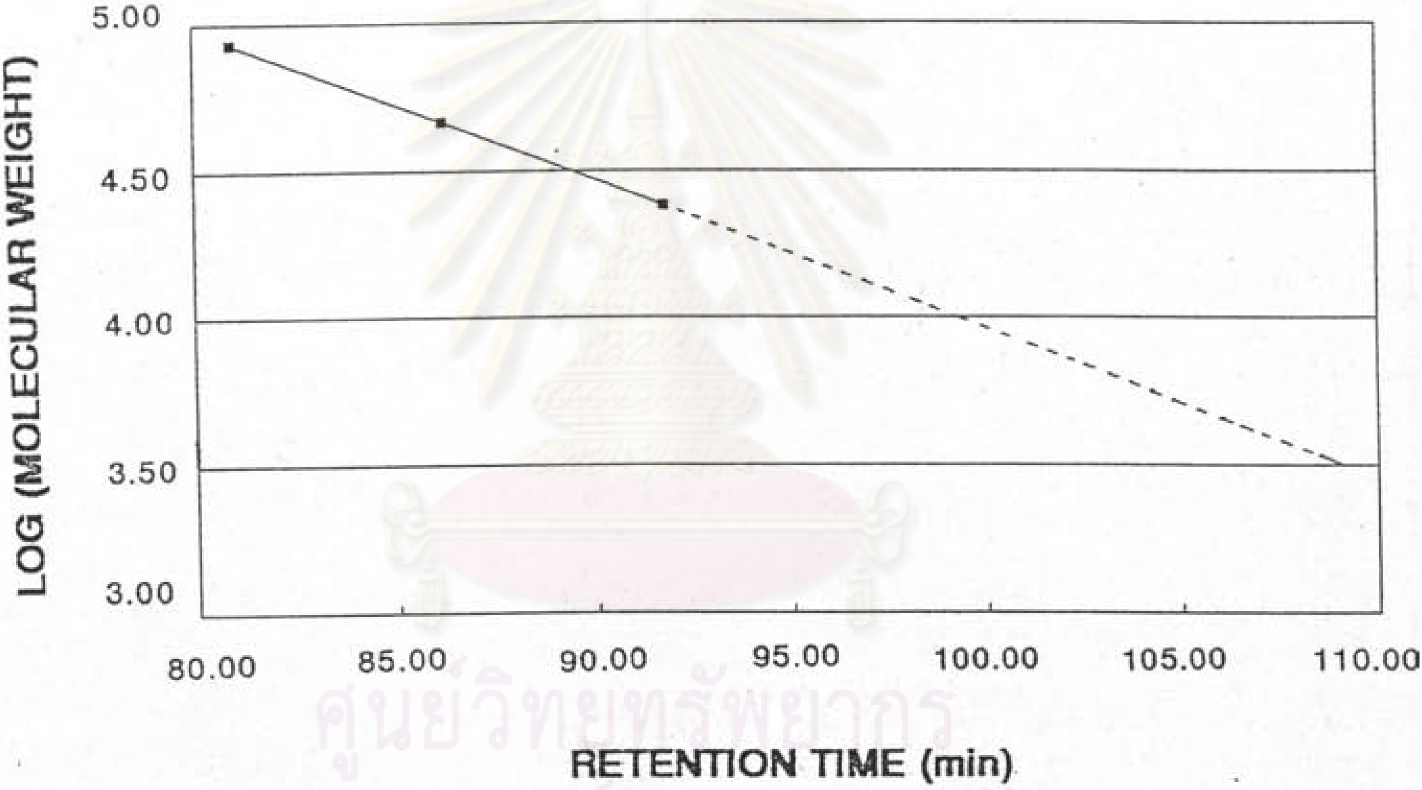

Figure 4.3 The molecular weight calibration curve of poly(ethylene oxide) standard

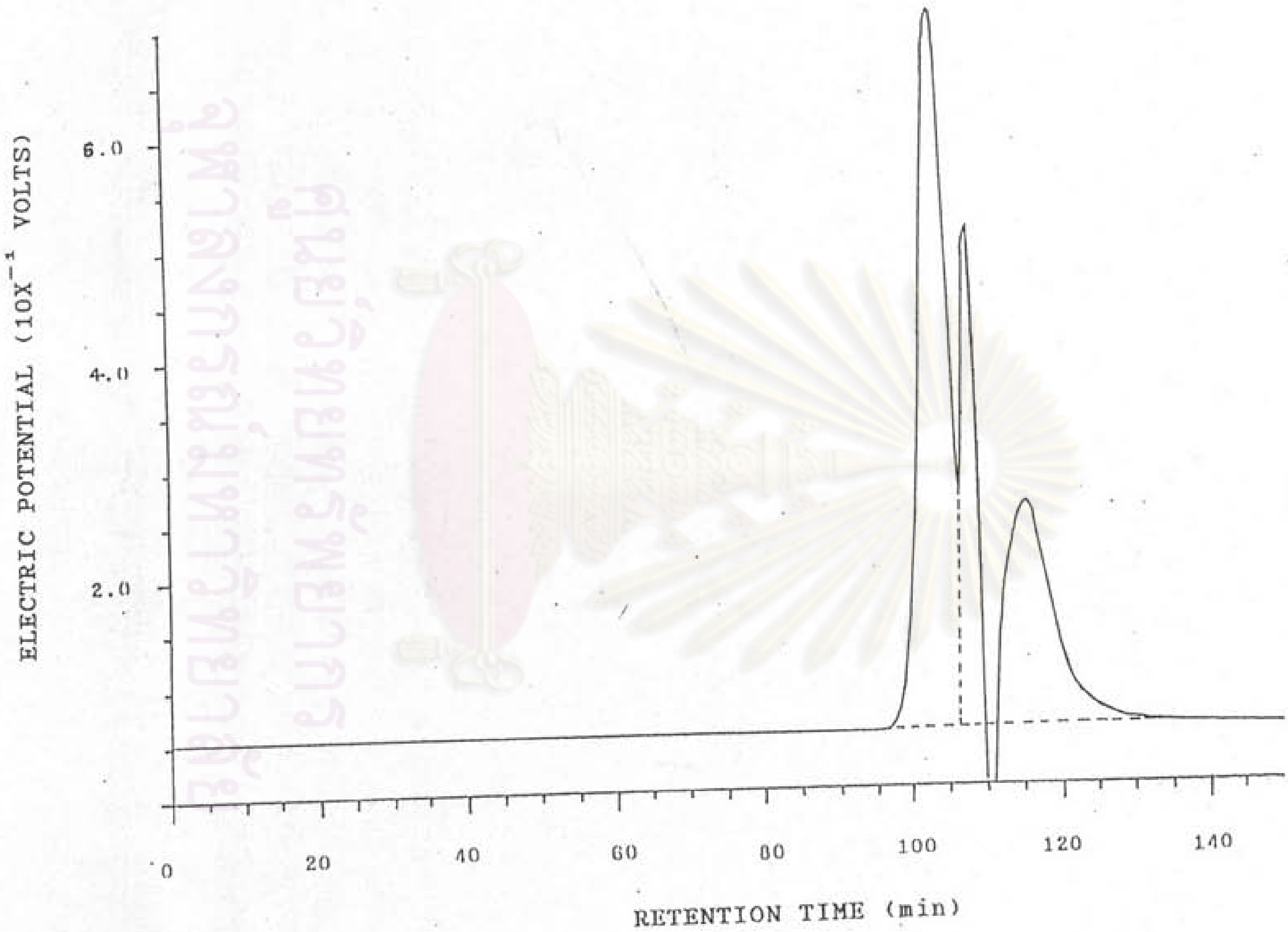

Figure 4.4 The GPC chromatograph of the graft polyacrylate chains

lic acid) with low molecular weights. The third peak is unknown molecules with average molecular weights of about 1570.

The GPC data of the saponified starch-g-poly(acrylic acid) copolymers show that the retention times are longer than those of poly(ethylene oxide) standards used in the molecular weight calibration curve. Thus, an approximate molecular weight of the grafted polyacrylate could only be determined by extrapolating the calibration curve of M.W. to the retention time range obtained from Appendixes B.1-B.3. By this method, the distribution of molecular weights of the graft polyacrylate calculated is in the ranges of 4,009-17,076 and 2,880-4,009.

The approximate molecular weights of the graft poly(acrylic acid) calculated by the extrapolation of calibration curve to the retention time range are in the range of 2,917-4,294 and 4,294-15,664 for the starch-g-poly(acrylic acid) copolymer synthesized by 2.95 M of acrylic acid, 0.2217 M [H_2O_2] and reaction temperature of 35°C. The degrees of polymerization of the graft poly(acrylic acid) are in the range of 40-218. The molecular weight is relatively low compared with the others in the literature reviewed in Chapter 2. This result can probably be due to the insufficient amount of monomer concentration to be grafted on the starch substrate.

4.3 Water Absorption of The Saponified Starch-g-Poly(acrylic acid) copolymers.

a) The mechanism of the reaction

The mechanism for the grafting polymerization of acrylic acid monomer (M) onto the cassava starch is shown below.

1 Redox sysrem

The free radicals ($R^{\cdot}$) are created by the oxidation reaction of ascorbic acid with hydrogen peroxide as shown in equation (2.28), there are some other reactions of wastage. When the reaction temperature increases, hydrogen peroxide decomposes to water and oxygen gas, a highly effective radical scavenger, as shown in equation (3.1). The oxygen molecules can then oxidise L(+) ascorbic acid to dehydroascorbic acid, a non-reactive species for the graft polymerization, as shown in equation (2.27).

2 Homopolymerization

The number of free radicals are responsible for the relative amounts of homopolymer and copolymer. The homopolymerization and graft polymerization take place simultaneously and competitively.

$$R^{\cdot} + M \longrightarrow RM^{\cdot} \qquad (4.2)$$

$$RM^{\bullet} + n\,M \longrightarrow RM^{\bullet}_{(n+1)} \qquad (4.3)$$

$$RM^{\bullet}_{(n+1)} + {}^{\bullet}R \longrightarrow \text{Homopolymer} \qquad (4.4)$$

$$RM^{\bullet}_{(n+1)} + {}^{\bullet}MR \longrightarrow \text{Homopolymer} \qquad (4.5)$$

3 Graft polymerization

$$R^{\bullet} + S\text{-}H\ (\text{starch}) \longrightarrow S^{\bullet} + R\text{-}H \qquad (4.6)$$

$$S^{\bullet} + nM \longrightarrow SM^{\bullet}_{n} \qquad (4.7)$$

$$SM_{n}^{\bullet} + RM^{\bullet}_{(n+1)} \longrightarrow \text{graft copolymer} \qquad (4.8)$$

$$SM_{n}^{\bullet} + R^{\bullet} \longrightarrow \text{graft copolymer} \qquad (4.9)$$

$$S^{\bullet} + RM^{\bullet}_{(n+1)} \longrightarrow \text{graft copolymer} \qquad (4.10)$$

4 Radical combination

$$R^{\bullet} + {}^{\bullet}R \longrightarrow RR \qquad (4.11)$$

$$R^{\bullet} + RM^{\bullet} \longrightarrow RMR \qquad (4.12)$$

b) The Homopolymer Determination

The water sorption of cassava starch was 0.48 g/g dry starch. The water absorption capacity of hydrolyzed stach-g-poly(acrylic acid) copolymers in deionized distilled water ranged from 19 to 234 times their original dried weight. Thus, these graft copolymers are high-water absorbing polymer as the difinition described by Kim, U.Y. (22). The high-water absorbing polymer is the material that absorbing capacity is greater than 15 times its own weight.

The reaction mixtures from the graft polymerization (with various starch/AA ratios) were precipitated in cold acetone. The precipitate was filtered and dried in the 65°C oven for 24 hours. The dried products were ground to a podwery form and then extracted PAA homopolymer by the Soxhlet extraction with methanol. The homopolymer content was found to be less than 2% and the water absorption of the extracted and saponified product was about 210 g/g dried weight as compared with the maximum water absorption of this product was 234 g/g dried weight.

There are not significantly different in the water absorptions of the extracted and non-extracted HSPAA copolymers. In addition, the potassium polyacrylate, the saponified product of PAA homopolymer, has the water absorption capacity as well. It is therefore not necessary to remove the homopolymer from the product before the product was saponified as described in Chapter 3.

4.3.1 Effect of Starch-to-Acrylic Acid Ratios.

The effect of starch/AA ratio on the water absorption of the saponified starch-g-PAA copolymer in deionized distillated water is tabulated in Table 4.1 and shown in Figure 4.4.

TABLE 4.1

Effect of the Concentration of Acrylic Acid on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymer in Deionized Distillated Water.

Starch(g) /Acrylic acid(M)[a]	Water absorption in deionized distillated water (g/g)
30 : 1.47	108.7
30 : 2.21	117.0
30 : 2.95	234.3
30 : 3.68	159.4
30 : 4.42	24.2

[a] Data were obtained under the following condition: $[H_2O_2]$ = 0.2217 M, [Ascorbic acid] = 0.004 M, reaction temperature = 35°C.

The experimental data show that the water absorption increases while the amount of AA increases from 1.47 to 2.95 M. When the content of AA used is higher than 2.95 M, the water absorption decreases. This result is perhaps explained in the term of the homopolymer content. The higher monomer concentration provides more homopolymerization reaction than copolymerization. This can be due to: (i) at high AA concentration, the radicals have a great opportunity to react with monomer molecules, thus producing several AA radicals with short kinetic chains. The kinetic chain length (ν) of a radical chain polymerization is defined as the average number of monomer molecules polymerized per each radical. The kinetic chain length is inversely dependent on the radical concentration. Increasing the radical concentrations in radical polymerization leads to smaller sized polymer molecules (81). These short propagating chains can either terminate by a coupling reaction between themselves or with a few active sites of the polymer substrate to get a very short graft; (ii) the difficulty of the monomer molecules to diffuse in the proximity of the polymeric substrate of starch.

The water absorption phenomena of an anionically high-water absorbing polymer has been elaborated by several investigators mentioned previously in Chapter 2. The results correlate quite well with the mechanistic model of the enhanced water sorbence of acrylate-grafted polysaccharides (82) which is essentially the same as the concepts of the swelling mechanism of gels originally proposed by Proctor (83). The important charcteristic of many gels is the presence of ionizable groups attached to the gel. When such a gel is placed in an ionic solution, an exchange of mobile ions takes place between the gel and the solution, but because of the presence of the bound groups, the mobile

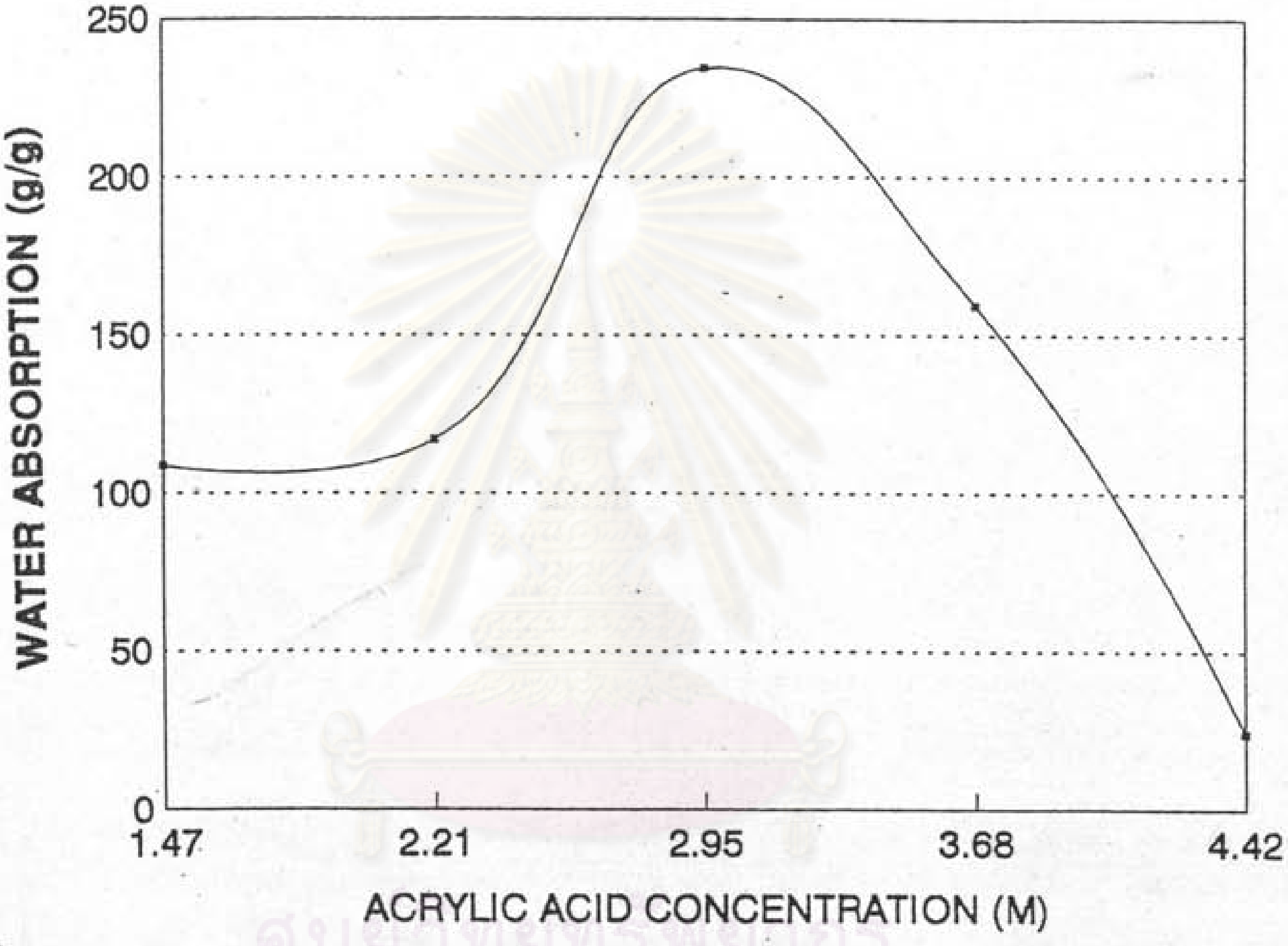

Figure 4.5 Effect of the concentration of acrylic acid on water absorption of saponified starch-g-poly(acrylic acid) copolymer in deionized distilled water.

ions are unevenly distributed in the gel containing the higher concentrations. The gel swells as a result of the entry of water in an attempt to reduce the osmotic pressure differential resulting from the difference in concentration of mobile ions between the interior of the gel and the external solution. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion brought about by the cohesive forces of the macromolecular network or the ion concentration between inside and outside the gel having reached equilibrium.

The mobile K^+ ions concentration in the grafted starch copolymer, resulting from the saponification step, is higher than that in deionized distilled water which consists of only hydrogen and oxygen atoms. As the ionic groups cannot move out of the copolymer, the solution within the copolymer is regarded as separated from the external solution by a semipermeable membrane which confines to the potassium carboxylate groups, but gives free passages to water. The copolymer swells as a result of the difference in ion concentrations. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion, i.e., when the ion concentration between inside and outside the copolymer has reached equilibrium.

Swelling of the hydrolyzed starch-g-PAA copolymer is the same as that of the ionic networks described by Flory (84). If the graft polymer chains contain ionizable groups, the swelling forces may be greatly increased as a result of the localization of the charges on the polymer chains. When the starch-g-PAA copolymer was neutralized with KOH, either partially or totally, the negatively charged carboxyl groups of the graft polymer chains set up an electrostatic repulsion which tends to expand the network. However, the exceedingly large electrostatic repulsions would prevail if the fixed carboxylate ions were only present; it may never be realized because of the inevitable presence of other ions ---the potassium ions, for example, and those of other solution which may be present (including ions from the solvent, e.g., H^+ and OH^- of water). These ions reduce the electrostatic repulsion tremendously as compared with what it would be when they are absence.

The exchange of ions and solution between the starch-g-PAA copolymer and the surrounding solution continues until the equilibrium between the swollen copolymer and its surroundings closely resembling Donan membrane equilibria is reached. The copolymer acts as its own membrane preventing the charged substituents, which are distributed essentially at random through the copolymer much as they would be in an ordinary solution, from diffusing into the outer solution. The swelling force resulting from the presence of the fixed charges may be identified with the swelling pressure, or net osmotic pressure, across the semipermeable membrane in a typical Donan equilibrium. The quantitative treatment of this force may be carried out in either of two ways. We first introduce the conditions for equilibrium between the mobile ion species inside and outside the copolymer in either case. According to one of the alternative procedures, the electric potential difference between the interior of the copolymer and its surroundings is calculated through consideration of the ionic equilibria. From the charge density in the copolymer and its potential relative to the outer solution, the Coulombic energy is easily computed, and from the latter the expansive force may be found. In the second method it is observed that the concentration of mobile ions will always be greater in the copolymer than outside because of, in qualitative terms, the attracting power of the fixed charges. Consequently, the osmotic pressure of the solution inside will exceed that of the external solution. The expansive force may be equated to this difference in osmotic pressure for the two solutions. The two methods yield identical results.

Okiemen and Ebhoaye (85) suggested that the water absorption properties of cellulosic materials are thought to result from the interaction through hydrogen bonding of the hydroxyl groups on the cellulose with water molecules.

It must be noted that the figures of water absorption capacity of the graft copolymer in deionized water change with multiple wetting-drying cycles. The loss of absorbency is probably due to a condensation type of crosslinking reaction occurring between hydroxyl and carboxyl substituents at the drying temperature (86).

4.3.2 Effect of Hydrogen Peroxide Concentration.

The effect of hydrogen peroxide concentration on the water absorption of the saponified starch-g-poly (acrylic acid) copolymers in deionized distilled water is tabulated in Table 4.2 and shown in Figure 4.6.

TABLE 4.2

Effect of the Hydrogen Peroxide Concentration on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymers in Deionized Distilled Water.

Hydrogen peroxide concentrations (M)	Water absorption in deionized distilled water (g/g)
0.0553	53.4
0.1107	152.0
0.1661	191.2
0.2217	234.3
0.2768	38.9
0.3322	18.5

* Data were obtained under the following condition: Starch/Acrylic acid ratio = 30:2.95 g/M, reaction temperature = 35°C, [Ascorbic acid] = 0.004 M.

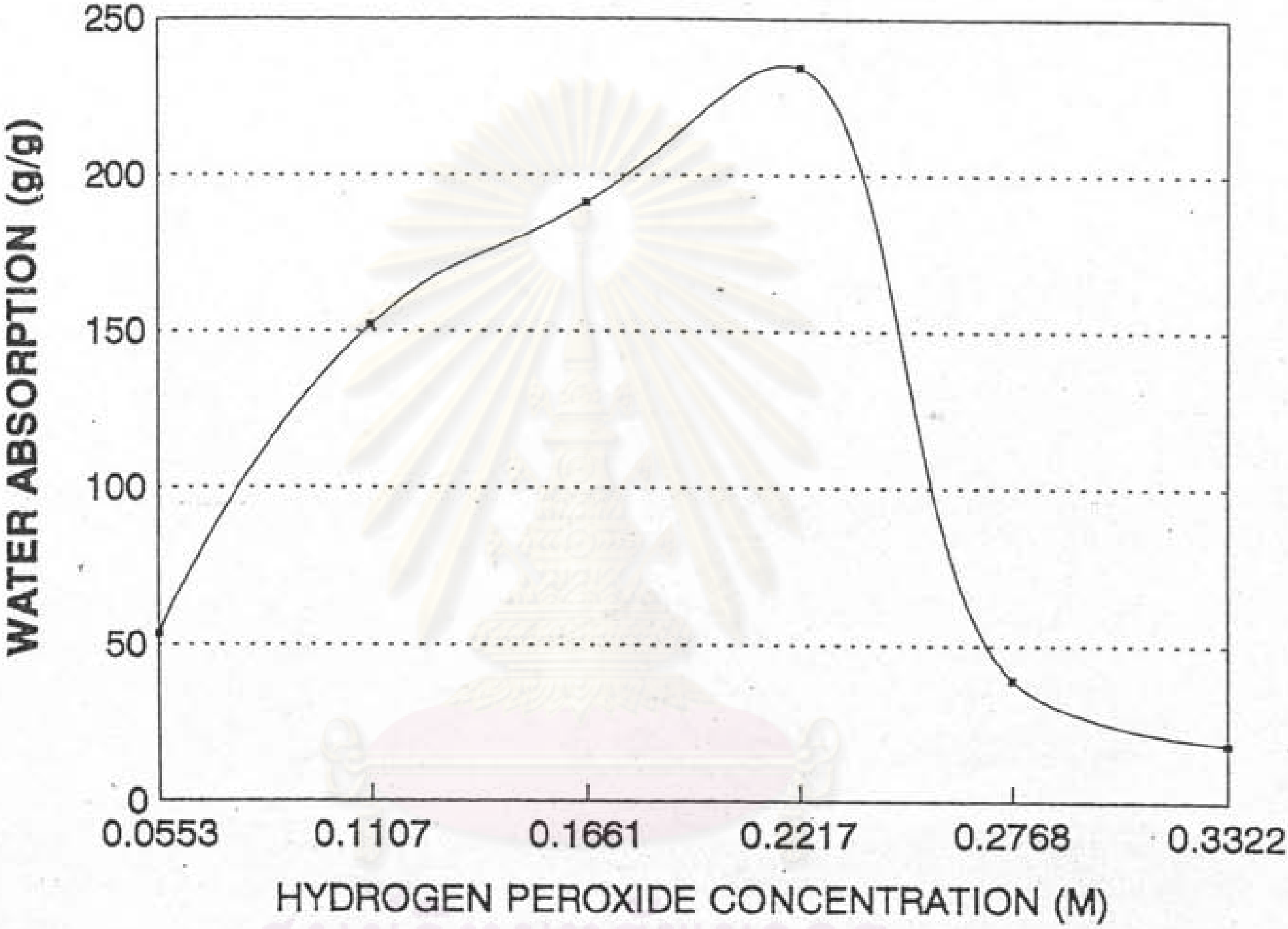

Figure 4.6 Effect of the concentration of hydrogen peroxide on water absorption of saponified starch-g-poly(acrylic acid) copolymer in deionized distilled water.

The experimental data shows that the water absorption increases until the hydrogen peroxide concentration increases to 0.2217 mole/litre, then it decreases gradually.

The effect of hydrogen peroxide concentration on the water absorption values is best explained in terms of the frequency of interposition of the grafted polyacrylate chains on the starch backbone (38). When the initiator concentration increases, the grafting frequency of polyacrylate also increases, but not all that straight forward, at the initiator concentrations higher than 0.2217 M, water absorption seems to decrease gradually. According to the concept of grafting frequency on water absorption capacity, one can speculate the possible mechanistic pathways that may occur as the following. As starch is a chunck polymer with a molecular weight average of over 10^6, it is then regarded as an immobile phase, i.e. only acrylic acid is mobile.

The most common case of radical chain polymerization can thereby be described by equation (4.13) which shows the polymerization rate to be dependent on the square root of the initiator concentration (87).

$$R_p = k_p [\mathrm{M}] \left(\frac{f k_d [\mathrm{I}]}{k_t} \right)^{1/2} \qquad (4.13)$$

It is quite evident that the initiator efficiency, f, in equation (4.13), governed by its concentration is one of the major attributes to rate of polymerization and its consequence to molecular weight. At the initiator concentrations below 0.2217 M, not enough initiator concentrations are present for graft copolymerization, resulting in a low grafting frequency in the starch-g-poly(acrylic acid) to fulfil the absorption phenomena described earlier. At the higher concentration of initiator, abundant initiator radicals are present in the reaction mixture. The radicals encounter the acrylic acid monomer easily than do with the starch chain. The consequence is a greater amount of homopolymer with low molecular weights due to the shorter kinetic chains. Nonetheless, if these acrylic acid propagating chains can encounter the starch substrate frequently, highly grafted starch will be another reaction product. Based on the absorption phenomena, too high a graft frequency will result in relatively low water absorption capacity. In addition, there is a possibility of radical recombination because of the collision of radicals before they have an opportunity to react with acrylic acid monomer or the starch backbone.

One very importnat fact should be borne in mind that the production of initiator radicals is also assisted by the co-initiator, ascorbic acid. With a fixed amount of the co-initiator, too high such an initiator, will normally be a waste.

4.3.3 Effect of Reaction Temperature.

The effect of reaction temperature on the water absorption of the saponified starch-g-poly(acrylic acid) copolymer in deionized distillated water is tabulated in Table 4.3 and shown in Figure 4.7.

TABLE 4.3

Effect of the Reaction Temperature on Water Absorption of the Saponified Starch-g-poly-(acrylic acid) Copolymers in Deionized Distillated Water[a].

Reaction temperature[a] (°C)	Water absorption in deionized distillated water (g/g)
35	234.3
45	72.6
55	51.4
65	40.9

[a] Data were obtained under the following condition: Starch/Acrylic acid = 30:2.95 g/M, $[H_2O_2]$ = 0.2217 M, [Ascorbic acid]= 0.004 M.

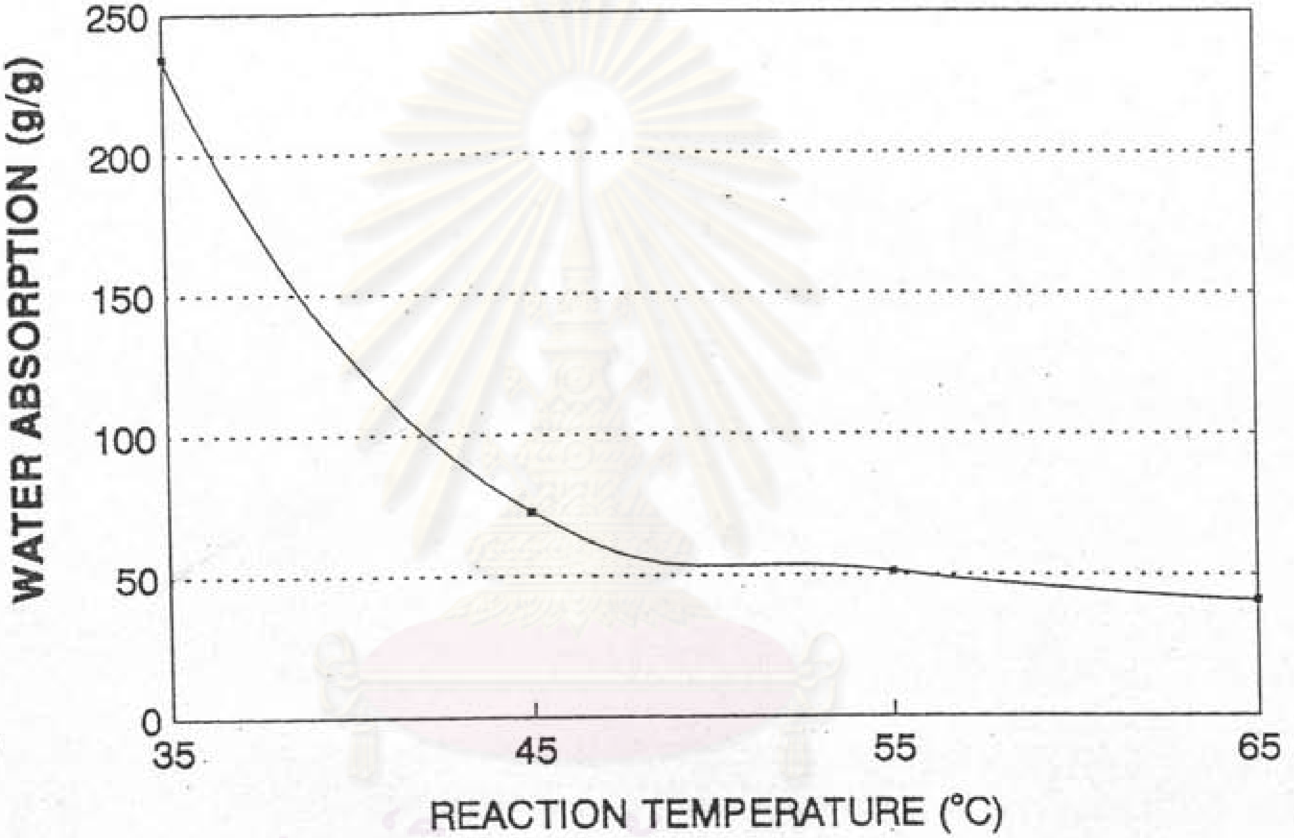

Figure 4.7 Effect of the reaction temperature on water absorption of saponified starch-g-poly(acrylic acid) copolymer in deionized distilled water.

The experimental data show that the water absorption decreases when the rection temperature increases. Increasing the reaction temperature is expected to cause the following phenomena. The rate of graft copolymerization decreases due to decreases in monomer and initiator concentrations in the swollen phase as the rate of consumption of the monomer due to homopolymerization is also higher at higher temperatures (88). In addition, less hydrogen peroxide concentrations are available for the graft copolymerization reaction because the decomposition of hydrogen peroxide also proceeds at a rate that increases approximately 2.2 times for each 10 degree rise in temperature over the range of 20-100°C (78). Volatility and decomposition of H_2O_2 are significantly high at higher temperature of the reactor. As already described in Chapter 2, the decomposition product of hydrogen peroxide is the oxygen gas which is a highly effective radical scavenger due to its extremely high inhibition constant. Besides the inhibiting effect, the oxygen molecules can oxidised L(+)-ascorbic acid, an accelerator for hydrogen peroxide, to dehydroascorbic acid, a non-reactive species for polymerizations. Upon the studies of these three basic parameters, it is indeed confident to state that the primary factor must be the temperature of reactor, otherwise, no initiator is available to induce any polymerization.

4.4 Effect of NaCl Solutions on Water Absorption of The Saponified Starch-g-poly(acrylic acid) copolymers.

4.4.1 Effect of Starch-to-Acrylic Acid Ratios.

The effect of the presence of NaCl solutions at the concentrations of 0.1, 0.5, 1.0, and 2.0% w/v on the water absorption is clearly illustrated in Table 4.4 and Figures 4.8-4.9. The water absorption efficiency of the saponified starch-g-poly(acrylic acid) copolymer is very dependent on the ion concentration. Indeed, the effect of NaCl at different concentrations shows a dramatic decrease in water absorption in the presence of ions.

The effect of salt concentration on the water retention values is best explained in terms of the swelling of modified starch containing anionic groups. This treament was first proposed by Proctor which was then extended and further clarified by Scallan and Grignon (89) in terms of swelling of such gels as described above. Briefly this approach may be summarized in the following way:

The ions attached to the macromolecular network in the gel are immobile and are considered to be saparated from the external solution by a semipermeable membrane, which confines to the immobile ions, but give passage to water and all simple ions. The excess concentration of mobile ions in the gel phase is calculated using Donnan's equilibrium model. This excess concentration is directly proportional to osmotic pressure differential, and this,

Table 4.4

Effect of the Concentration of Acrylic Acid on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymer in NaCl Solutions of 0.1, 0.5, 1.0, 2.0% w/v

Starch(g)/Acrylic acid(M)	Water Absorption (g/g) in NaCl solutions of			
	0.1%[a]	0.5%[b]	1.0%[c]	2.0%[d]
30:1.47	39.6	33.3	28.9	23.2
30:2.21	42.1	37.7	32.3	27.4
30:2.95	133.6	104.7	90.9	58.9
30:3.68	58.4	42.7	35.6	31.2
30:4.42	18.2	12.7	10.9	10.1

[a] $[Na^+]=[Cl^-]=0.017$, $[Na^+]+[Cl^-] = 0.034$ mole-ion/dm^3, ionic strength = 0.017 M.

[b] $[Na^+]=[Cl^-]=0.085$, $[Na^+]+[Cl^-] = 0.170$ mole-ion/dm^3, ionic strength = 0.085 M.

[c] $[Na^+]=[Cl^-]=0.171$, $[Na^+]+[Cl^-] = 0.342$ mole-ion/dm^3, ionic strength = 0.171 M.

[d] $[Na^+]=[Cl^-]=0.342$, $[Na^+]+[Cl^-] = 0.684$ mole-ion/dm^3, ionic strength = 0.342 M .

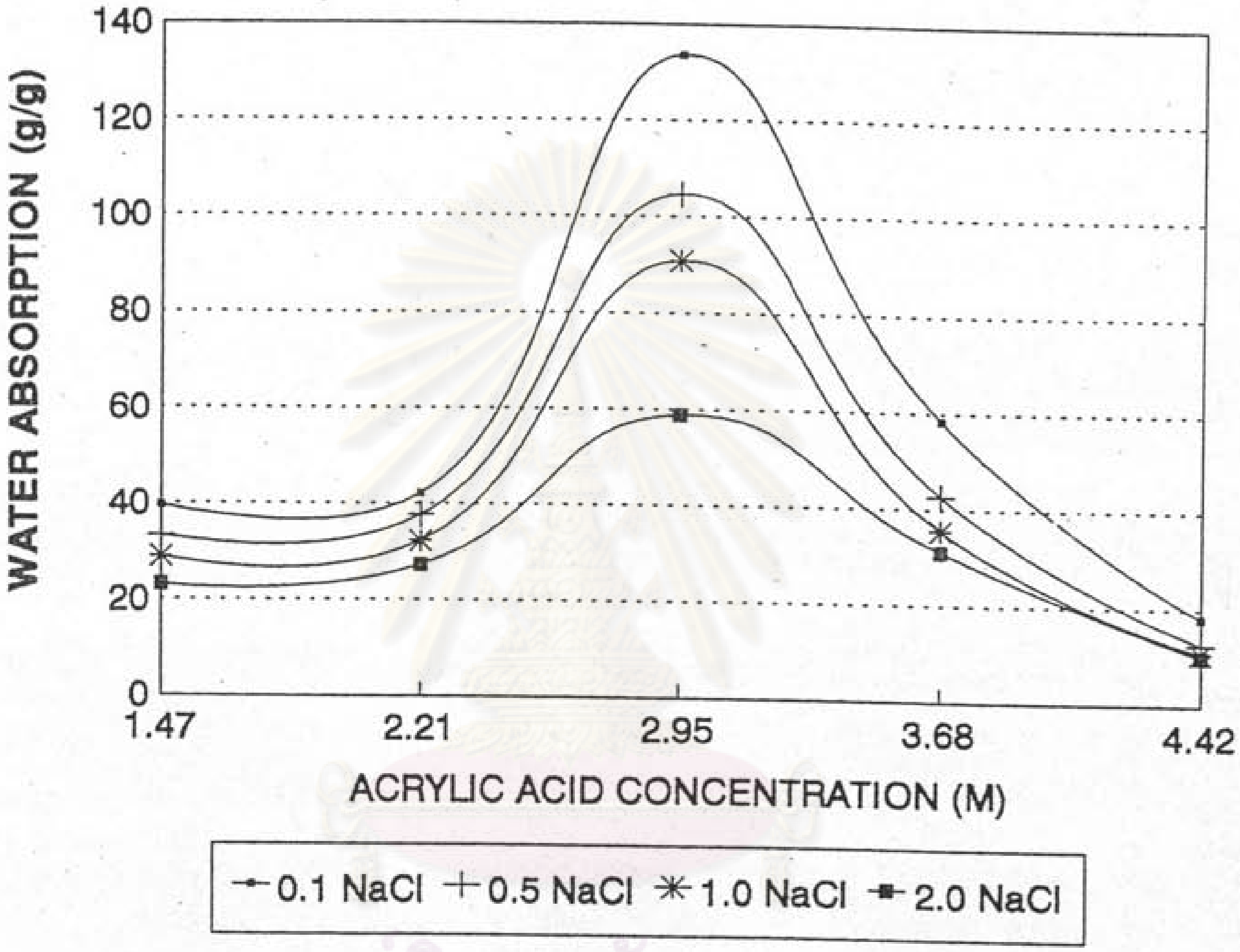

Figure 4.8 Effect of the concentration of acrylic acid on water absorption of saponified starch-g-poly(acrylic acid) copolymer in NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v.

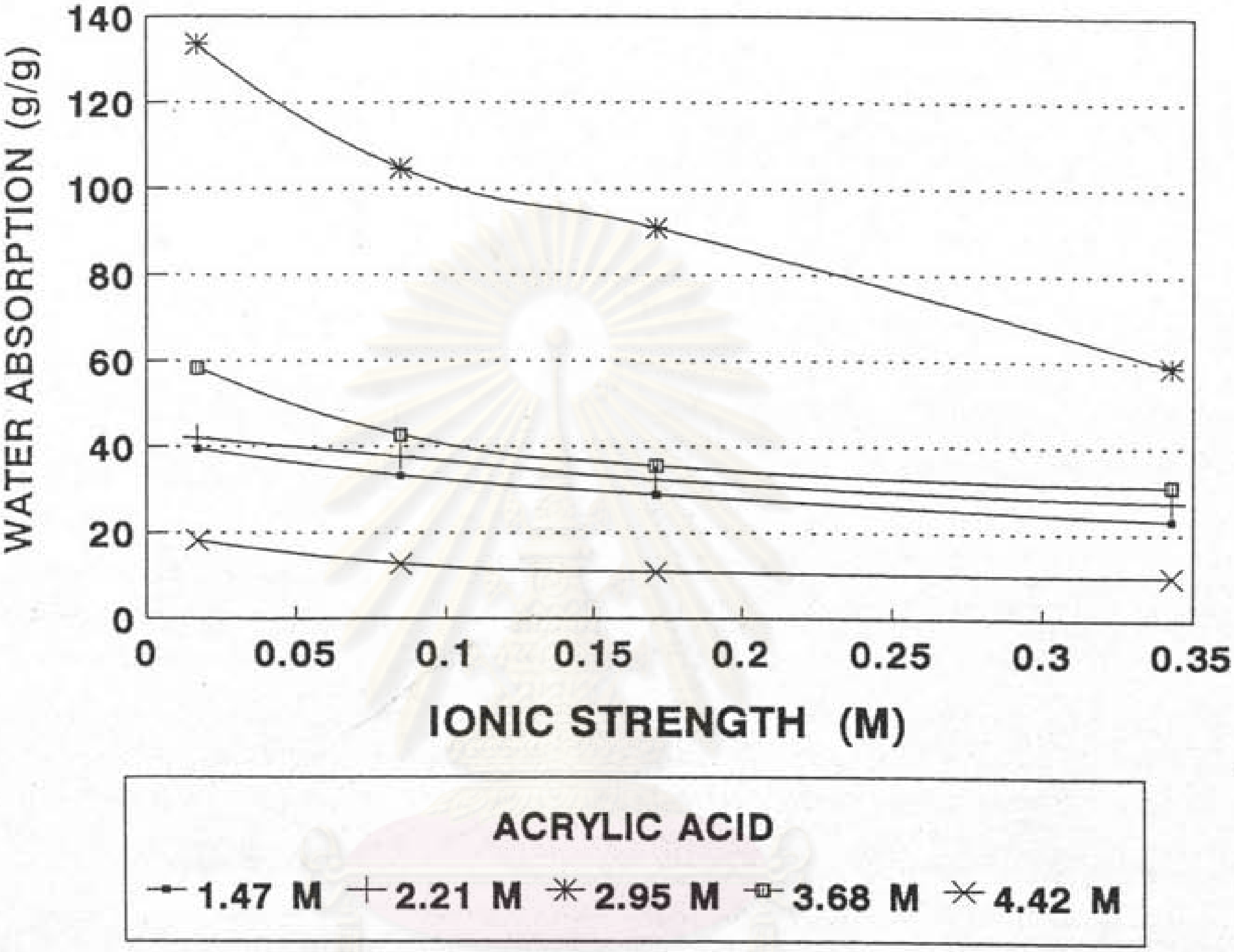

Figure 4.9 Effect of the ionic strengths of NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various acrylic acid concentrations.

in turn, is assumed to be directly proportional to a degree of swelling, i.e., to the water sorption itself (90).

In this case the graft copolymer is present as the anion of potassium salt (polycarboxylate), which is assumed to be a strong electrolyte. Saponified starch graft copolymer was placed in NaCl solutions. At the surface of this material the behavior as semipermeable membrane exists. To maintain electrical neutrality on the both sizes of the membrane, Na^+ and Cl^- ions have diffused through the membrane from external solution to the interior of copolymers. The amount of NaCl diffused from external solution to the interior of copolymer is inversely proportional to the concentration of non-diffusible ion, polycarboxylate. This unequal distribution of the diffusible ions (Na^+ and Cl^-) in the two compartments is the result of the Donnan effect (91), assume that saponified starch graft copolymer has the same behavior as the sodium salt of protein.

The osmotic pressure of this system is now determined by the difference between the number of particles in the external solution and that in the interior of the copolymers. Assume that K^+ ions in the interior of the copolymers have the same concentration (mole-ion/dm^3) as that of polycarboxylate.

Then,

$$\Pi = \frac{(2a^2 + 2ab)RT}{a + 2b} \qquad (4.14)$$

where

Π : osmotic pressure, atm;

a : concentration of polycarboxylate and K^+ ions in the interior of the copolymer, mole-ion-dm^{-3};

b : concentration of Na^+ and Cl^- ions in the external solution, mole-ion-dm^{-3};

R : gas constant, 8.314 J $K^{-1}mol^{-1}$;

T : temperature, K.

According to eq. (4.14), as the concentration of salt solution increases, the osmotic pressure of this system would then decrease. The more ions are present, the less water is absorbed. In soil environment, a similar effect is expected as soils contain various types of ions and plant nutrients. The use of fertilizer in agriculture, horticulture, and arboriculture also has imposed such an effect, a reduction in water absorption. In order to compensate for the decrease in water intake, the use of more superabsorbent polymer is therefore necessary.

4.4.2 Effect of Hydrogen Peroxide Concentration.

The effect of the presence of NaCl solution at the concentrations of 0.1, 0.5, 1.0, and 2.0% w/v on the water absorption is clearly illustrated in Table 4.5 and Figures 4.10-4.11.

The experimental data show that the effect of NaCl at different concentrations dramatically decreases water absorption in the presence of ions. The more NaCl concentration in solution is used, The less water absorption is obtained. Likewise, this phenomenon is best explained in terms of the swelling of modified starch containing anionic groups as described above.

4.4.3 Effect of Reaction Temperature.

The effect of NaCl solution at the concentrations of 0.1, 0.5, 1.0, and 2.0% w/v on the water absorption is clearly illustrated in Table 4.6 and Figures 4.12-4.13.

The experimental data show that the effect of NaCl at different concentrations shows a dramatic decrease in water absorption. The more NaCl concentration in solution is used, the less water absorption is obtained. Similarly, this phenomena are best explained in terms of the swelling of modified starch containing anionic groups as described above.

Table 4.5

Effect of the Hydrogen Peroxide Concentration on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymers in NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v

Hydrogen peroxide concentration (M)	Water Absorption (g/g) in NaCl solutions of			
	0.1%[a]	0.5%[b]	1.0%[c]	2.0%[d]
0.0553	39.4	28.7	22.9	21.8
0.1107	51.0	42.3	38.1	34.4
0.1661	85.0	76.6	65.5	39.5
0.2217	133.6	104.7	90.9	58.9
0.2768	20.6	18.2	17.4	16.8
0.3322	12.75	10.92	10.15	9.93

[a] $[Na^+]=[Cl^-]=0.017$, $[Na^+]+[Cl^-] = 0.034$ mole-ion/dm^3. ionic strength = 0.017 M.

[b] $[Na^+]=[Cl^-]=0.085$, $[Na^+]+[Cl^-] = 0.170$ mole-ion/dm^3, ionic strength = 0.085 M.

[c] $[Na^+]=[Cl^-]=0.171$, $[Na^+]+[Cl^-] = 0.342$ mole-ion/dm^3, ionic strength = 0.171 M.

[d] $[Na^+]=[Cl^-]=0.342$, $[Na^+]+[Cl^-] = 0.684$ mole-ion/dm^3, ionic strength = 0.342 M.

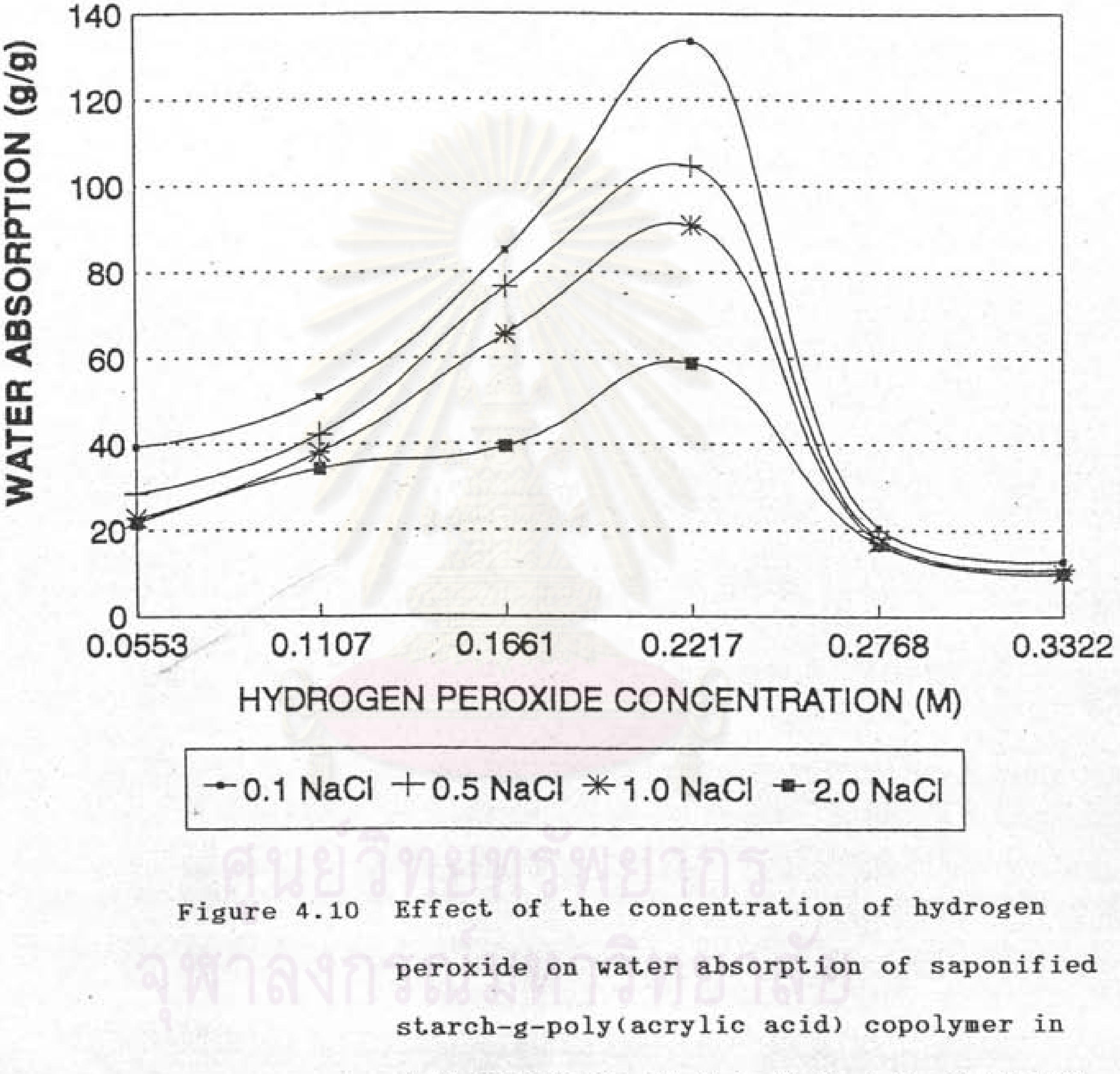

Figure 4.10 Effect of the concentration of hydrogen peroxide on water absorption of saponified starch-g-poly(acrylic acid) copolymer in NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v.

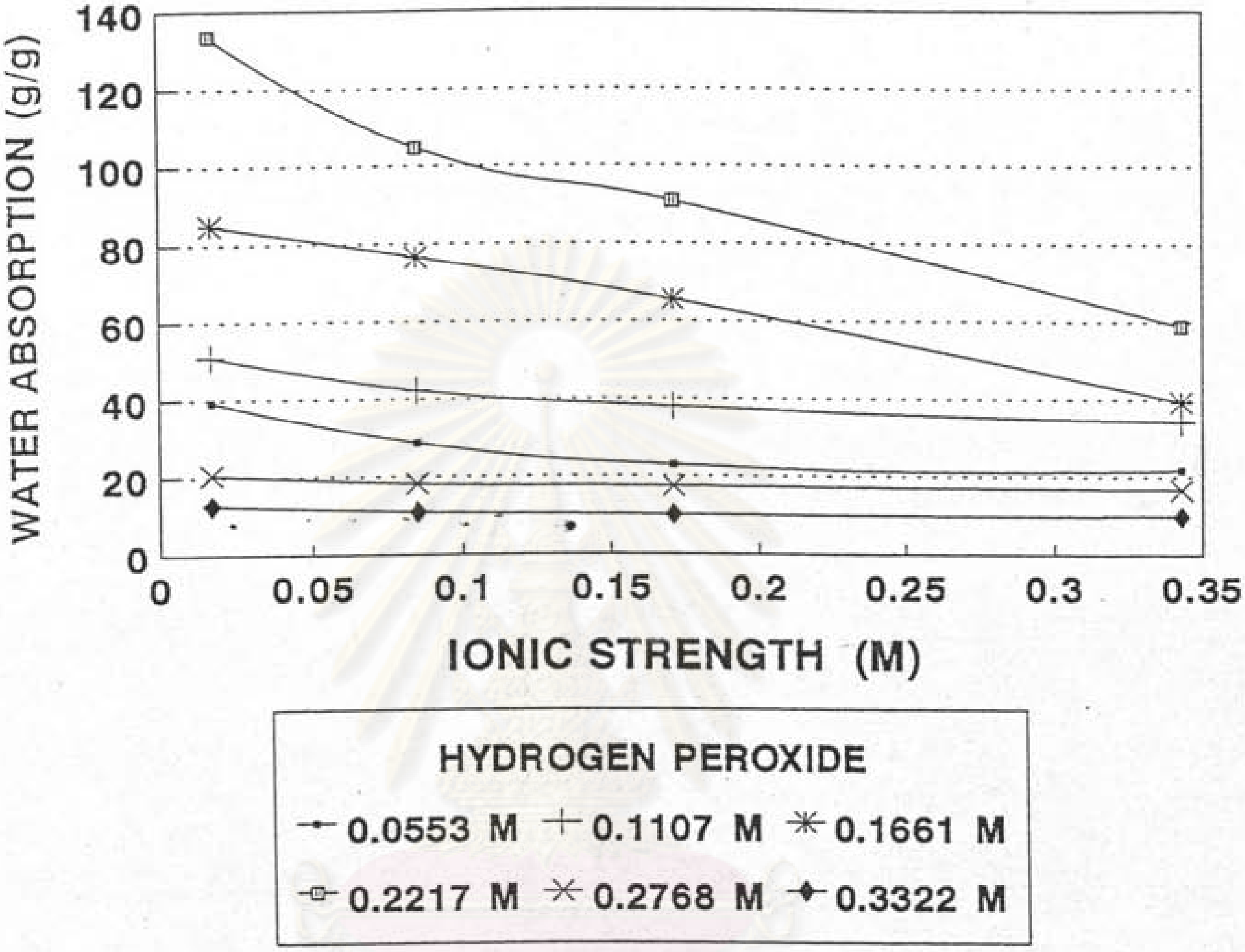

Figure 4.11 Effect of the ionic strengths of NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various hydrogen peroxide concentrations.

Table 4.6

Effect of the Reaction Temperature on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymers in NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v

Reaction temperature (°C)	Water Absorption (g/g) in NaCl solutions of			
	0.1%[a]	0.5%[b]	1.0%[c]	2.0%[d]
35	133.6	104.7	90.9	58.9
45	57.9	45.3	39.1	25.4
55	29.2	22.9	19.7	19.2
65	22.5	17.6	15.2	14.8

[a] $[Na^+]=[Cl^-]=0.017$, $[Na^+]+[Cl^-] = 0.034$ mole-ion/dm^3, ionic strength = 0.017 M.

[b] $[Na^+]=[Cl^-]=0.085$, $[Na^+]+[Cl^-] = 0.170$ mole-ion/dm^3, ionic strength = 0.085 M.

[c] $[Na^+]=[Cl^-]=0.171$, $[Na^+]+[Cl^-] = 0.342$ mole-ion/dm^3, ionic strength = 0.171 M.

[d] $[Na^+]=[Cl^-]=0.342$, $[Na^+]+[Cl^-] = 0.684$ mole-ion/dm^3, ionic strength = 0.342 M.

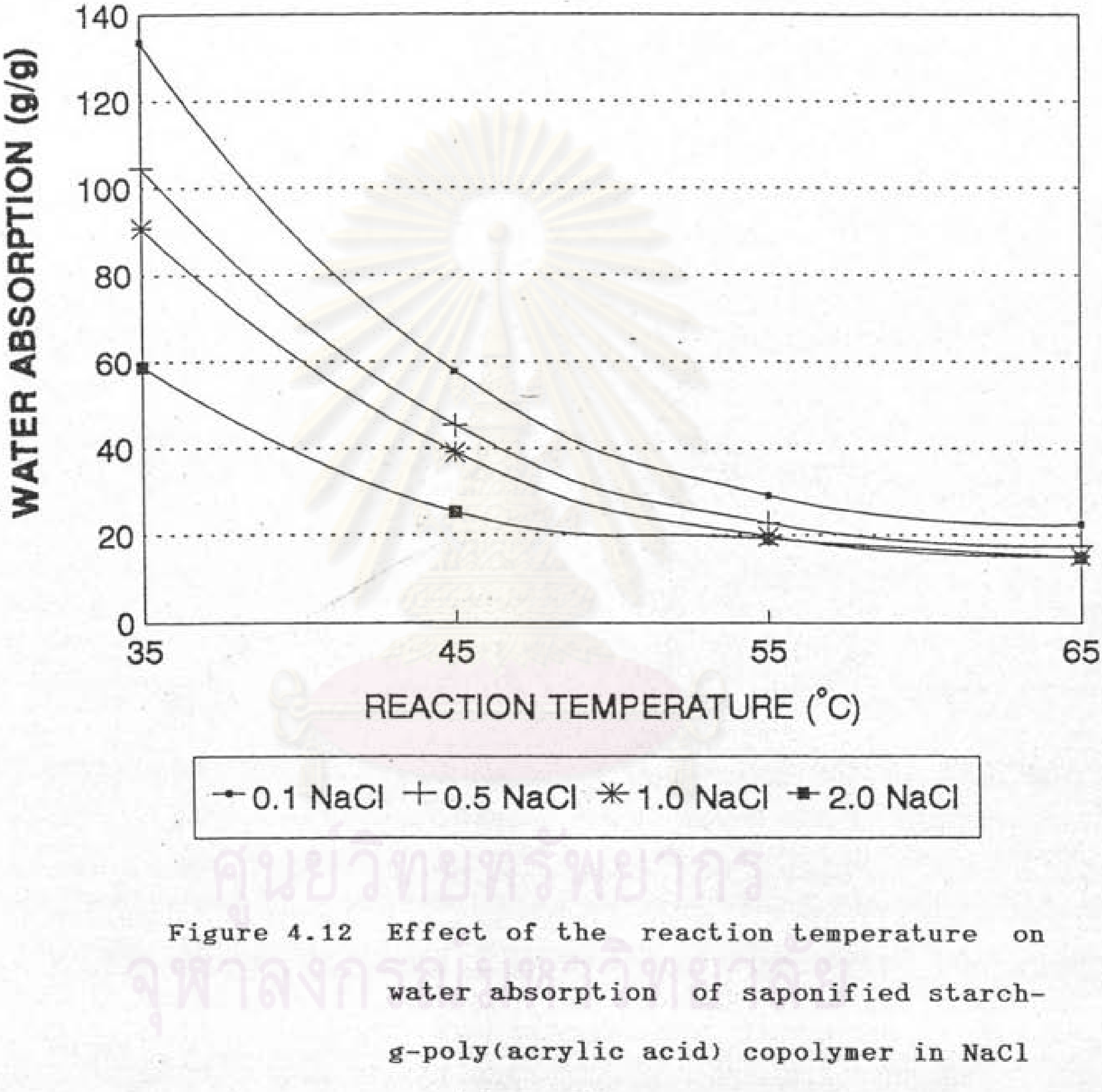

Figure 4.12 Effect of the reaction temperature on water absorption of saponified starch-g-poly(acrylic acid) copolymer in NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v.

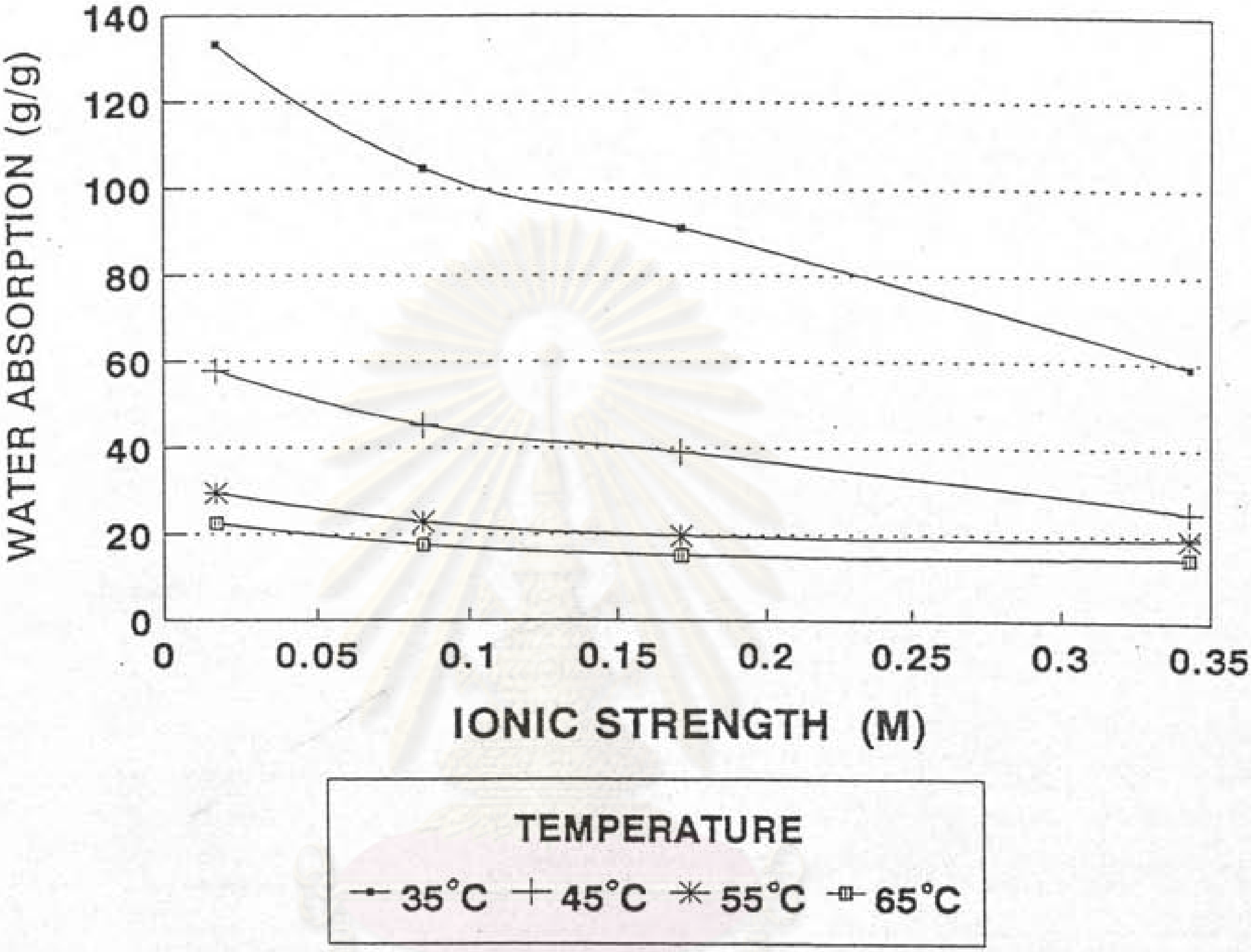

Figure 4.13 Effect of the ionic strengths of NaCl solutions of 0.1, 0.5, 1.0, 2.0% w/v on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various reaction temperatures.

4.5 Effect of $MgCl_2$ Solutions on Water Absorption of The Saponified Starch-g-poly(acrylic acid) copolymers.

4.5.1 Effect of Starch-to-Acrylic Acid Ratios.

The water absorption of the saponified starch-g-poly(acrylic acid) copolymers in 0.1, 0.5, 1.0, and 2.0% w/v of magnesium chloride concentrations is given in Table 4.7 and Figures 4.14-4.15.

On observing the case of $MgCl_2$, the water absorption decreased even more with increasing magnesium chloride concentrations. However, the curves of 0.5, 1.0, and 2.0% $MgCl_2$ concentrations are almost identical, except the 0.5% addition having a slightly higher water absorption only. This suggests that the osmotic pressure is reached ealier in the presence of the divalent ion. This decrease in water absorption can be due to the complexing ability of carboxylate groups inducing intramolecular and intermolecular complexes formation. consequently, the crosslink density increases. As a consequence, the absorption with $MgCl_2$ solution is much less than that does with NaCl. Here the high-est water intake of $MgCl_2$ solution is less than 57 g/g, while that of NaCl the value obtained is about 133 g/g, exceeding an absorption factor of 2.

TABLE 4.7

Effect of the Concentration of Acrylic Acid on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymer in $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v

Starch(g)/Acrylic acid(M)	Water Absorption (g/g) in $MgCl_2$ solutions of			
	0.1%[a]	0.5%[b]	1.0%[c]	2.0%[d]
30:1.47	30.8	16.9	15.9	15.6
30:2.21	32.9	17.9	17.1	16.6
30:2.95	56.1	25.0	19.5	18.9
30:3.68	42.8	19.5	17.4	16.9
30:4.42	12.7	9.9	8.7	8.0

[a] $[Mg^{+2}]=0.010$, $[Cl^{-}]=0.021$, $[Mg^{+2}]+[Cl^{-}]=0.031$ mole-ion/dm^3, ionic strength = 0.031 M.

[b] $[Mg^{+2}]=0.052$, $[Cl^{-}]=0.105$, $[Mg^{+2}]+[Cl^{-}]=0.157$ mole-ion/dm^3, ionic strength = 0.157 M.

[c] $[Mg^{+2}]=0.105$, $[Cl^{-}]=0.210$, $[Mg^{+2}]+[Cl^{-}]=0.315$ mole-ion/dm^3, ionic strength = 0.315 M.

[d] $[Mg^{+2}]=0.210$, $[Cl^{-}]=0.420$, $[Mg^{+2}]+[Cl^{-}]=0.630$ mole-ion/dm^3, ionic strength = 0.630 M.

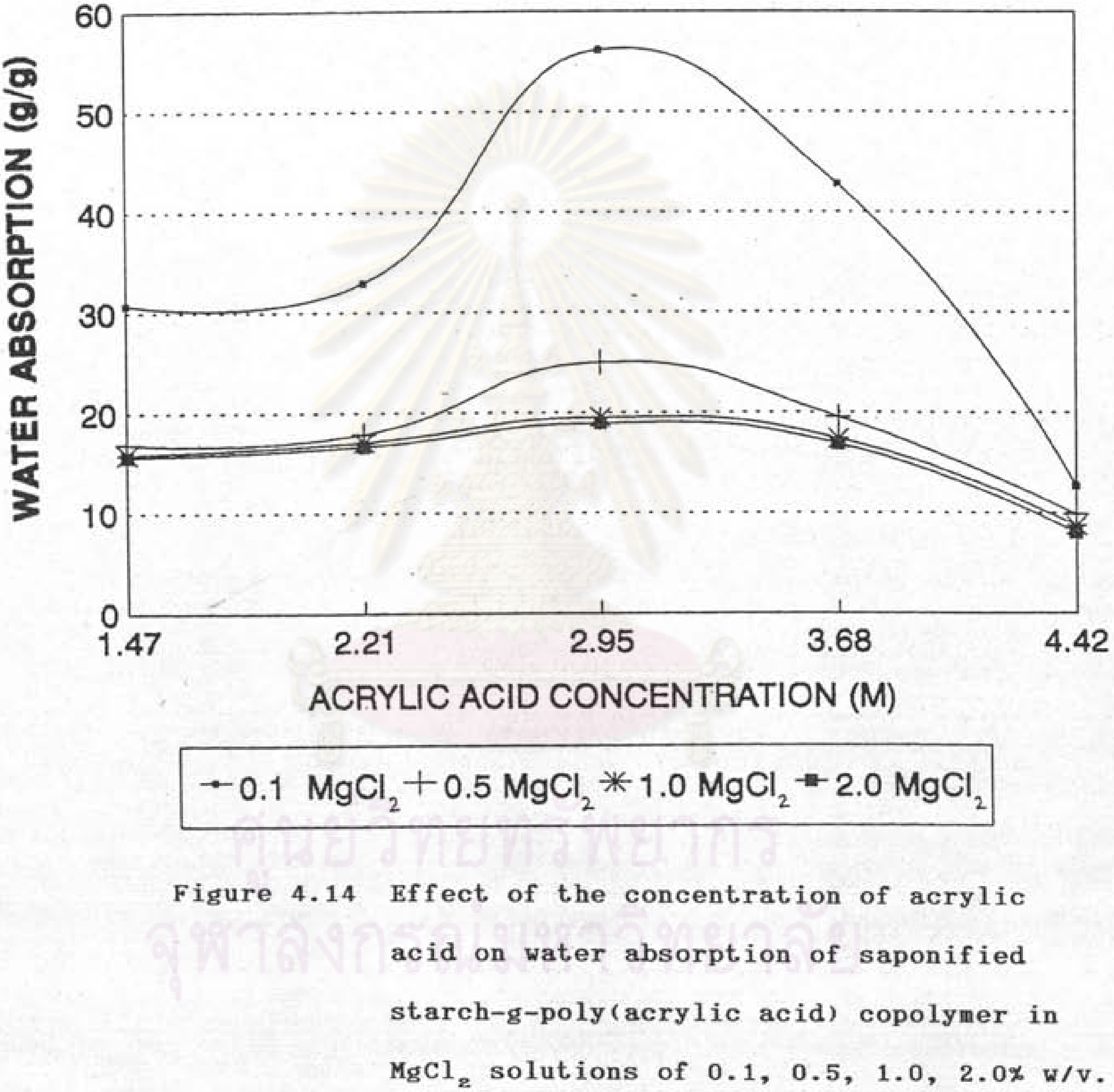

Figure 4.14 Effect of the concentration of acrylic acid on water absorption of saponified starch-g-poly(acrylic acid) copolymer in $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v.

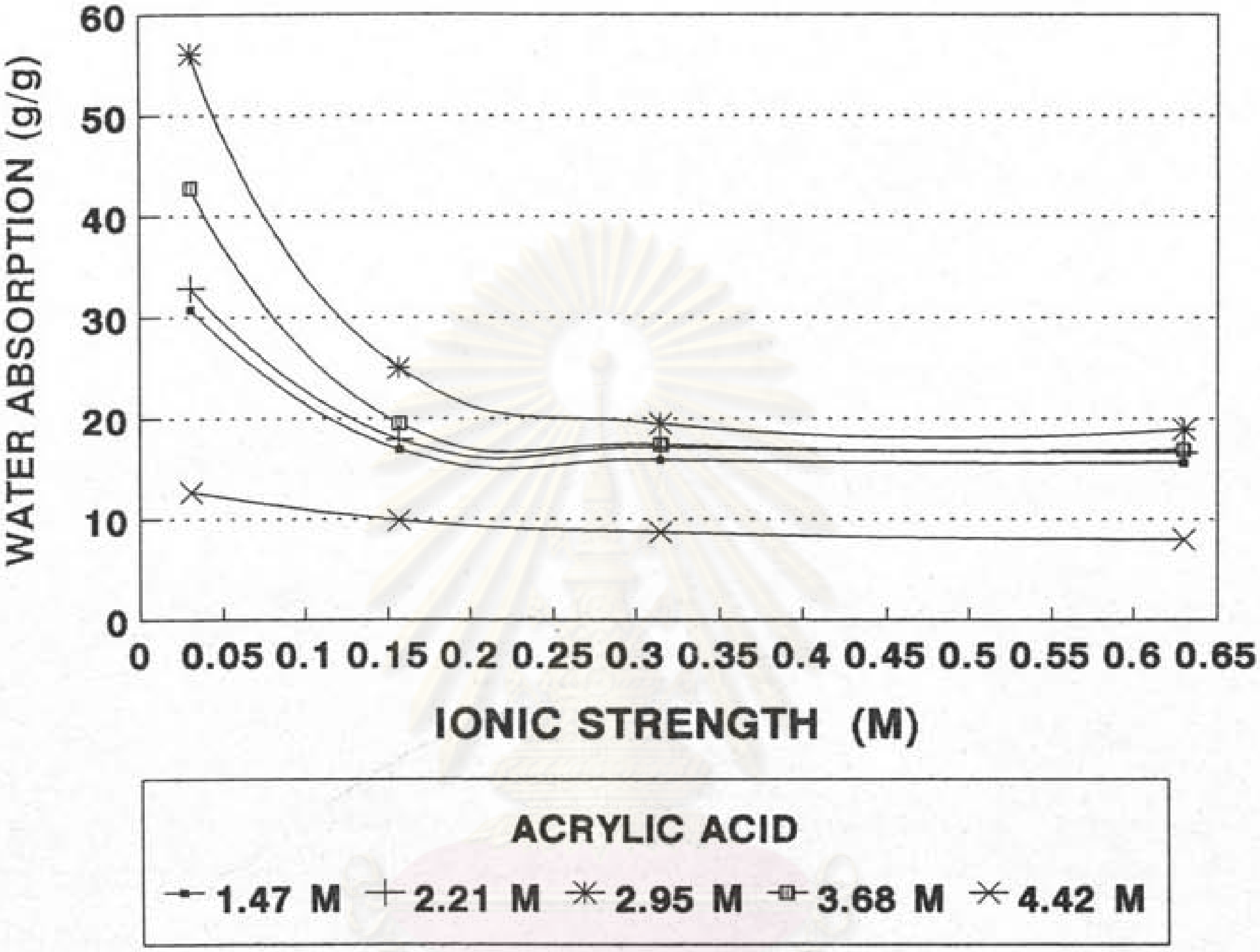

Figure 4.15 Effect of the ionic strengths of $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various acrylic acid concentrations.

The water absorption of the hydrolyzed starch-g-PAA copolymer in deionized distillated water as compared to the water absorptions of 0.5% w/v of NaCl and $MgCl_2$ is shown in Figure 4.16. At the concentration of 0.5% w/v of NaCl and $MgCl_2$ their coresponding ionic concentrations (ionic strengths) are 0.171 and 0.157 (0.085 and 0.157 M) mole-ion/dm^3 respectively. Considering the graft copolymer as a function of the amount of acrylic acid, the absorption in deionized distillated water and salt solution exhibits the same pattern. The figure indicates an increase in absorption in lower concentrations of saline solutions. The salt effect is clearly evidenced as a result of the osmotic pressure differential between the internal and external solution of the copolymer, due to the different ion concentrations (46). The water intake by the copolymer reduced the osmotic pressure until an ionic concentration equilibrium was reached.

In addition, the effect of monovalent (Na^+) and divalent (Mg^{+2}) cations on the water absorption of the hydrolyzed starch-g-Poly(acrylic acid) copolymer in NaCl and $MgCl_2$ solutions is shown in Figure 4.7. At the same concentration, magnesium chloride solutions impose a lower absorption value than those of sodium chloride solutions. The decrease of absorption is due to screening of the ionic charges bound to the starch grafted copolymer and to the decrease of the osmotic pressure difference between the copolymer and the external solution when the ionic strength increases (92). The effect of the ionic strength on the swelling has been determined using the relation suggested by Hermans:

$$Q_e^{5/3} = A + Bi^2/I \qquad (4.15)$$

$$I = \tfrac{1}{2} \sum_i C_i z_i^2 \qquad (4.16)$$

where

Q_e = the retention at equilibrium;

i = the concentration of the charges bound to the copolymer;

I = the ionic strength of the external solution;

A and B = empirical parameters.

c_i = the concentration of the i^{th} ion

z_i = the charge of the i^{th} ion

The ionic strength of the solution depends on both the mobile ion concentration and their valency. Small quantities of divalent ions can decrease drastically the the swelling values. The decrease of absorption in magnesium chloride can be due to the complexing ability of the carboxylate groups inducing intramolecular and intermolecular complexes formation. Consequently, the crosslink density of the starch grafted copolymer increases.

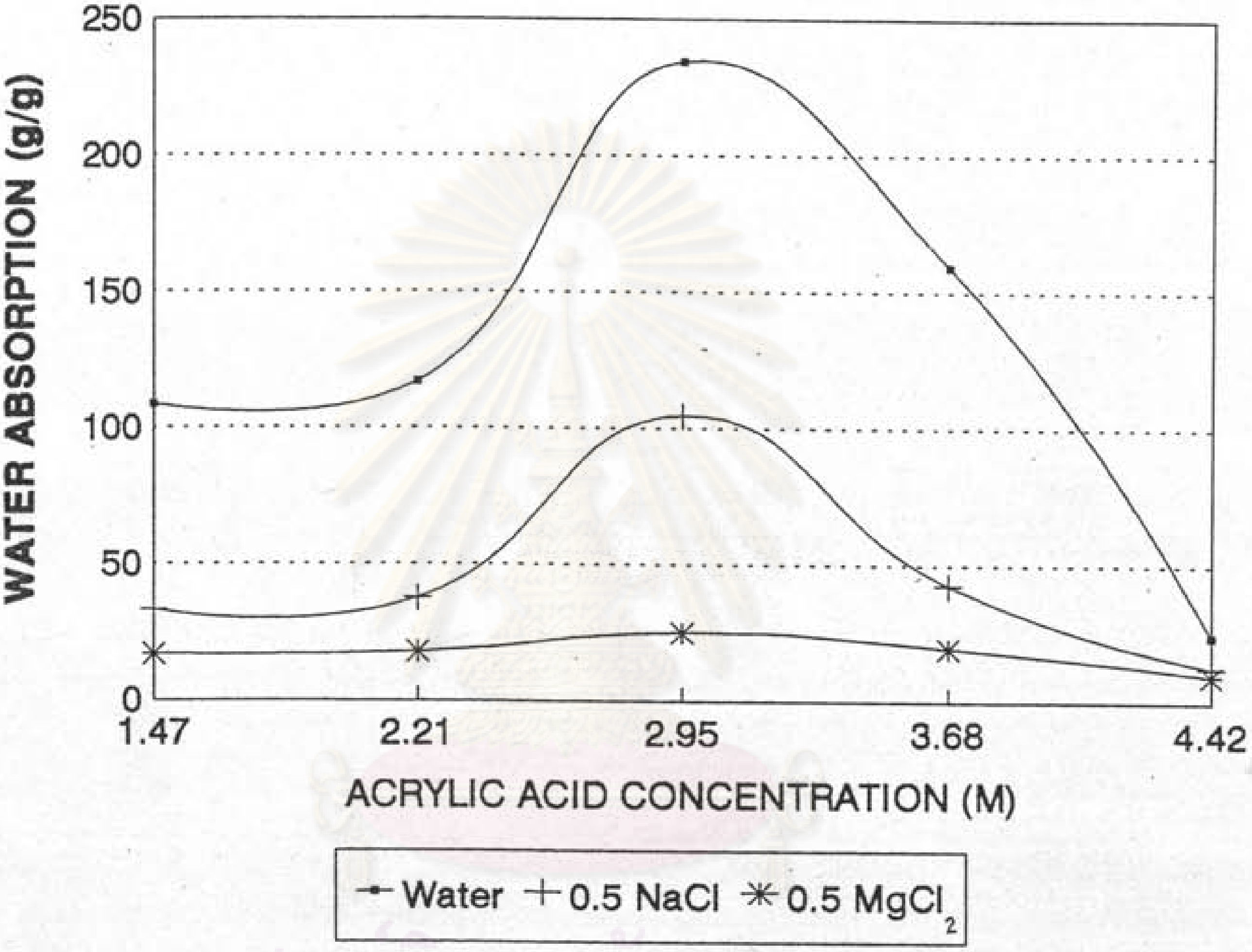

Figure 4.16 Comparative water absorption of hydrolyzed starch-g-poly(acrylic acid) copolymer between deionized distilled water and 0.5% w/v solutions of NaCl and $MgCl_2$.

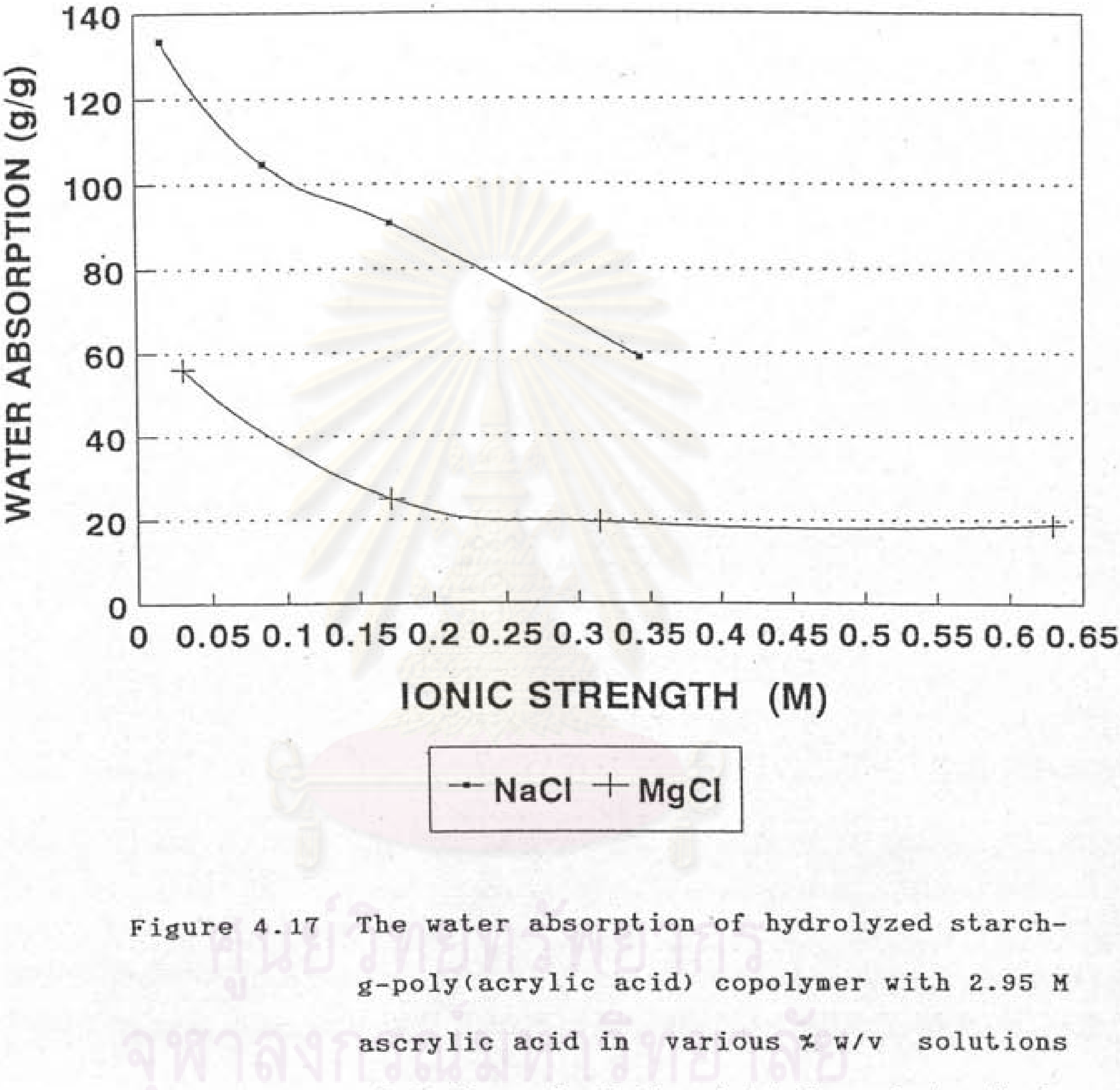

Figure 4.17 The water absorption of hydrolyzed starch-g-poly(acrylic acid) copolymer with 2.95 M ascrylic acid in various % w/v solutions of NaCl and $MgCl_2$ plotted against their ionic strength s.

4.5.2 Effect of Hydrogen Peroxide Concentration.

The effect of H_2O_2 concentration on the water absorption of the saponified starch-g-PAA copolymer in various $MgCl_2$ solutions is tabulated in Table 4.8 and shown in Figures 4.18-4.19.

The experimental data show that the effect of $MgCl_2$ at different concentrations dramatically decreases water absorption in the presence of ions. The higher the $MgCl_2$ concentration in solution, the lesser the water absorption. This phenomenon is also best explained in terms of the swelling of modified starch containing anionic groups as described above in 4.5.1.

4.5.3 Effect of Reaction Temperature.

The effect of reaction temperature on the water absorption of the saponified starch-g-poly(acrylic acid) copolymer in various magnesium chloride solutions is tabulated in Table 4.9 and shown in Figures 4.20-4.21.

The experimental data show that the effect of $MgCl_2$ at different concentrations dramatically decreases water absorption of the superabsorbents. The higher the $MgCl_2$ concentration in the solution is, The lesser the water absorption. This phenomenon is best explained in terms of the swelling of the modified starch containing anionic groups as described above in 4.5.1.

TABLE 4.8

Effect of the Hydrogen Peroxide Concentration on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymers in $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v

Hydrogen peroxide concentration (M)	Water Absorption (g/g) in $MgCl_2$ solutions of			
	0.1%[a]	0.5%[b]	1.0%[c]	2.0%[d]
0.0553	22.0	16.8	15.3	14.7
0.1107	28.4	18.2	17.8	17.5
0.1661	34.1	21.0	18.1	17.8
0.2217	56.1	25.0	19.5	18.9
0.2768	15.9	12.6	12.2	12.1
0.3322	10.3	9.3	9.0	9.0

[a] $[Mg^{+2}]=0.010$, $[Cl^-]=0.021$, $[Mg^{+2}]+[Cl^-]=0.031$ mole-ion/dm^3, ionic strength = 0.031 M.

[b] $[Mg^{+2}]=0.052$, $[Cl^-]=0.105$, $[Mg^{+2}]+[Cl^-]=0.157$ mole-ion/dm^3, ionic strength = 0.157 M.

[c] $[Mg^{+2}]=0.105$, $[Cl^-]=0.210$, $[Mg^{+2}]+[Cl^-]=0.315$ mole-ion/dm^3, ionic strength = 0.315 M.

[d] $[Mg^{+2}]=0.210$, $[Cl^-]=0.420$, $[Mg^{+2}]+[Cl^-]=0.630$ mole-ion/dm^3, ionic strength = 0.630 M.

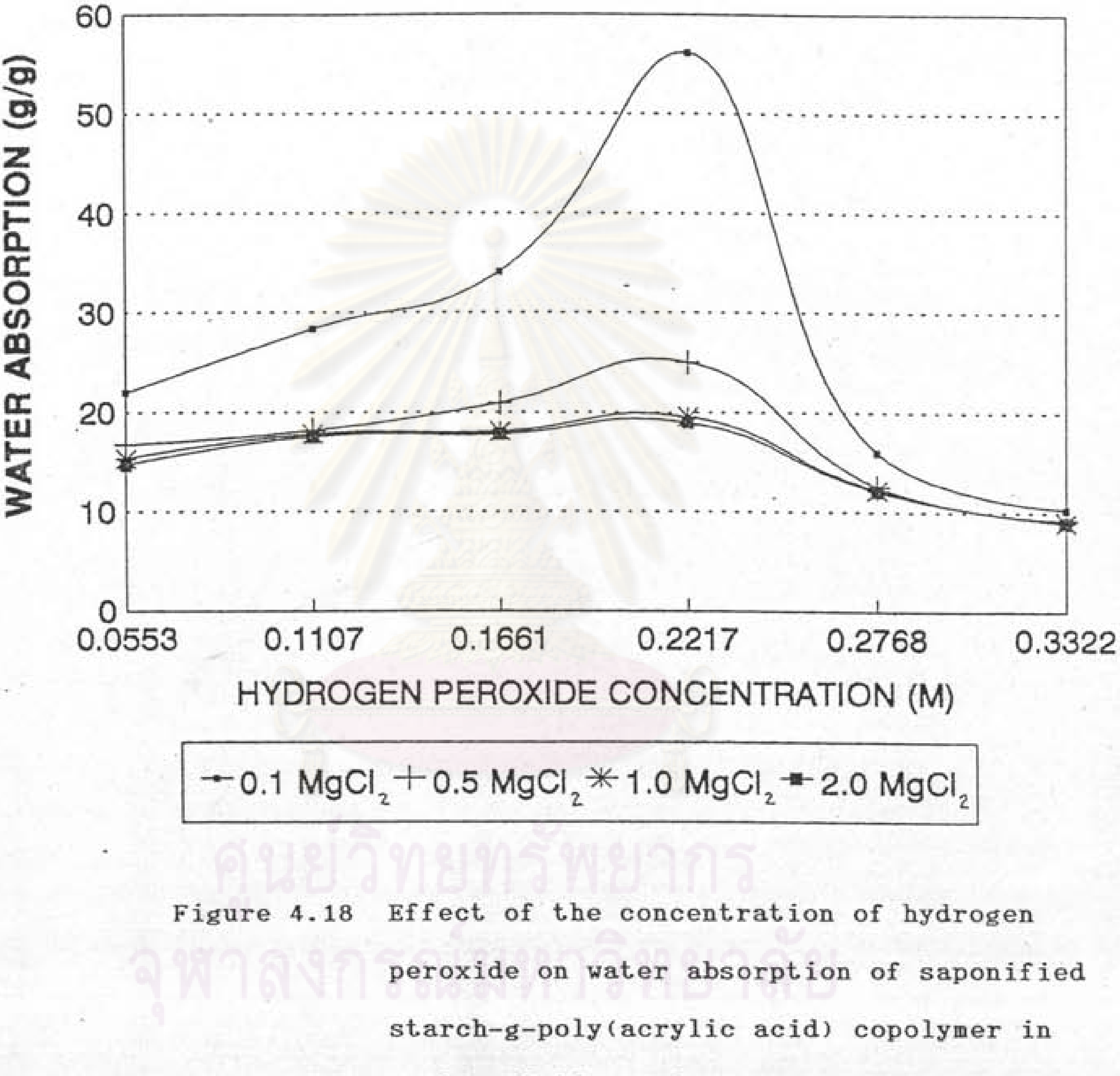

Figure 4.18 Effect of the concentration of hydrogen peroxide on water absorption of saponified starch-g-poly(acrylic acid) copolymer in $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v.

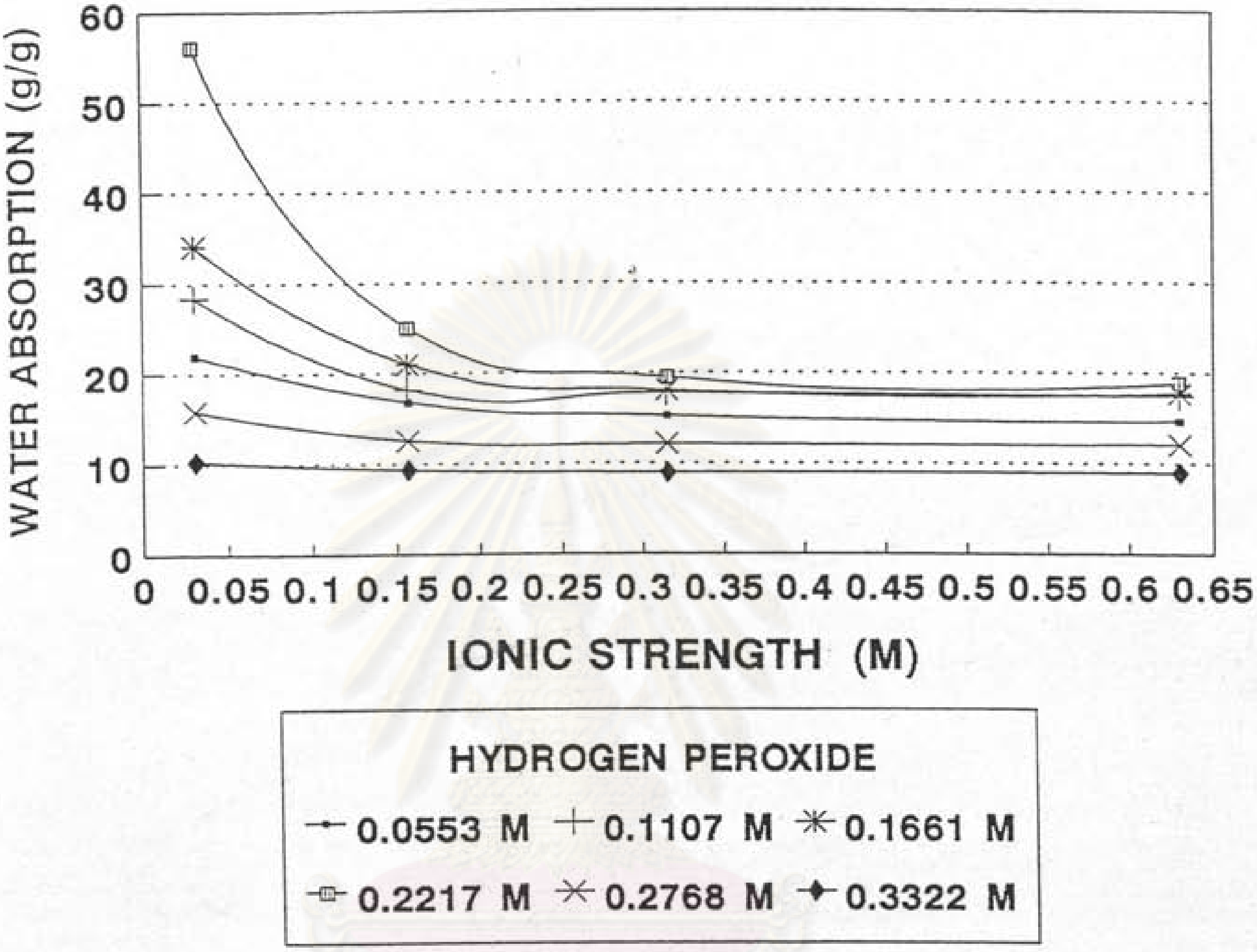

Figure 4.19 Effect of the ionic strengths of $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various hydrogen peroxide concentrations.

TABLE 4.9

Effect of the Reaction Temperature on Water Absorption of the Saponified Starch-g-poly-(acrylic acid) Copolymers in $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v

Reaction temperature (°C)	Water Absorption (g/g) in $MgCl_2$ solutions of			
	0.1%[a]	0.5%[b]	1.0%[c]	2.0%[d]
35	56.1	25.0	19.5	18.9
45	32.4	17.9	16.1	15.6
55	24.1	17.5	15.8	15.4
65	20.5	17.4	15.2	14.8

[a] $[Mg^{+2}]=0.010$, $[Cl^-]=0.021$, $[Mg^{+2}]+[Cl^-]=0.031$ mole-ion/dm^3, ionic strength = 0.031 M.

[b] $[Mg^{+2}]=0.052$, $[Cl^-]=0.105$, $[Mg^{+2}]+[Cl^-]=0.157$ mole-ion/dm^3, ionic strength = 0.157 M.

[c] $[Mg^{+2}]=0.105$, $[Cl^-]=0.210$, $[Mg^{+2}]+[Cl^-]=0.315$ mole-ion/dm^3, ionic strength = 0.315 M.

[d] $[Mg^{+2}]=0.210$, $[Cl^-]=0.420$, $[Mg^{+2}]+[Cl^-]=0.630$ mole-ion/dm^3, ionic strength = 0.630 M.

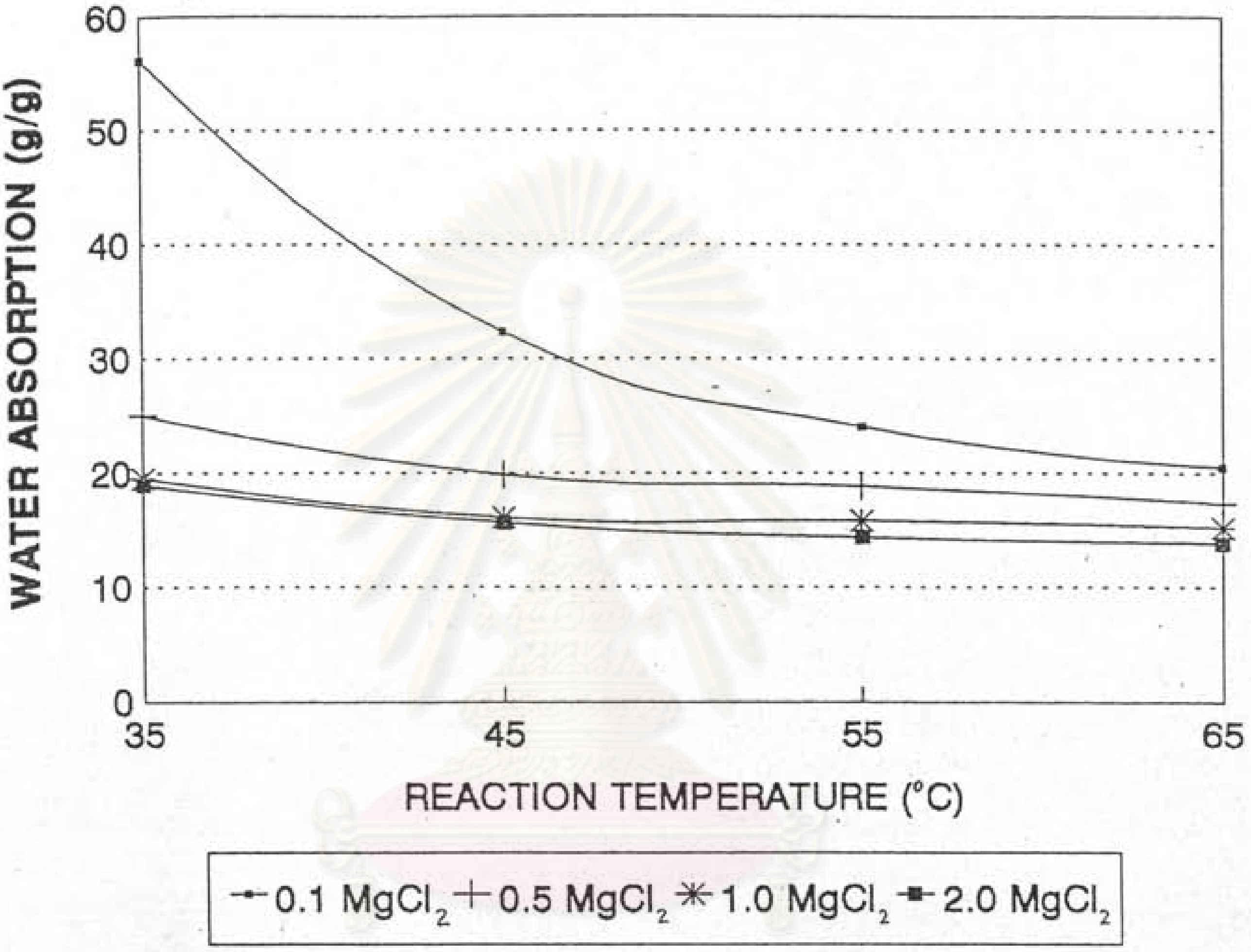

Figure 4.20 Effect of the reaction temperature on water absorption of saponified starch-g-poly(acrylic acid) copolymer in $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v.

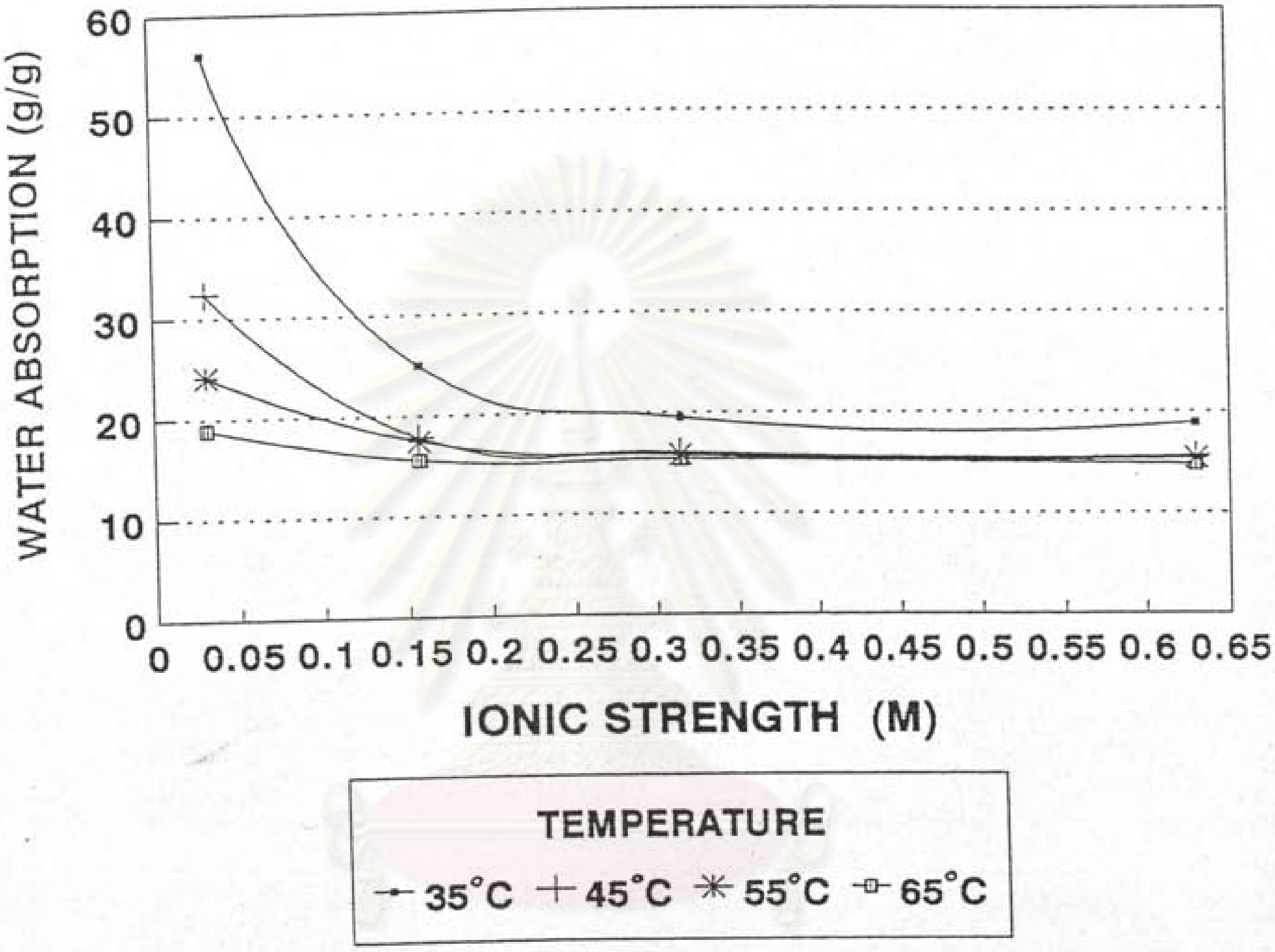

Figure 4.21 Effect of the ionic strengths of $MgCl_2$ solutions of 0.1, 0.5, 1.0, 2.0% w/v on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various reaction temperatures.

4.6 Effect of $K_3PO_4 . 3H_2O$, KCl, NH_4Cl and $(NH_4)_2HPO_4$ Solutions on Water Absorption of the Saponified Starch-g-Poly(acrylic acid) Copolymers.

4.6.1 Effect of Starch-to-Acrylic Acid Ratios.

The water absorption of the graft copolymer in the presence of $K_3PO_4.3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ is given in Table 4.10 and Figure 4.22-4.23. All of these salts have the concentration of 0.9% w/w, as it is the isotonic point of living organisms.

The result in the following table shows that water absorption decreases in relation to that of deionized distilled water. The water absorbency of the saponified starch-g-poly(acrylic acid) copolymer is presumably dependent upon the following three factors:

a) the osmotic pressure;

b) the molecular chain expansion resulting from repulsion between the electrolyte anions in the polymer chains;

c) the extent of crosslink affecting the degree of swelling of the polymer;

The absorbency (Q) can be expressed by the Flory's equation shown as following:

TABLE 4.10

Effect of the Concentration of Acrylic Acid on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymer in $K_3PO_4.3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ Solutions with an Identical Concentration of 0.9% w/w

Starch(g) /Acrylic acid (M)	Water absorption in $K_3PO_4.3H_2O$[a] (g/g) (0.204)	Water absorption in KCl[b] (g/g) (0.121)	Water absorption in NH_4Cl[c] (g/g) (0.168)	Water absorption in $(NH_4)_2HPO_4$[d] (g/g) (0.204)
30:1.47	26.3	28.8	20.7	24.9
30:2.21	30.6	34.0	25.3	27.6
30:2.95	56.6	62.8	37.9	51.5
30:3.68	37.6	40.9	29.5	32.4
30:4.42	10.6	11.3	9.3	10.1

[a] $[K^+]=0.101$, $[PO_4^{-3}]=0.034$, $[K^+]+[PO_4^{-3}] = 0.135$ mole-ion/dm^3, ionic strength = 0.2035 M.

[b] $[K^+]=[Cl^-]=0.121$, $[K^+]+[Cl^-] = 0.242$ mole-ion/dm^3, ionoic strength = 0.1210 M.

[c] $[NH_4^+]=[Cl^-]=0.168$, $[NH_4^+]+[Cl^-] = 0.336$ mole-ion/dm^3, ionic strength = 0.1680 M.

[d] $[NH_4^+]=0.136$, $[HPO_4^{-2}]=0.068$, $[NH_4^+]+[HPO_4^{-2}] = 0.204$ mole-ion/dm^3, ionic strength = 0.2040 M.

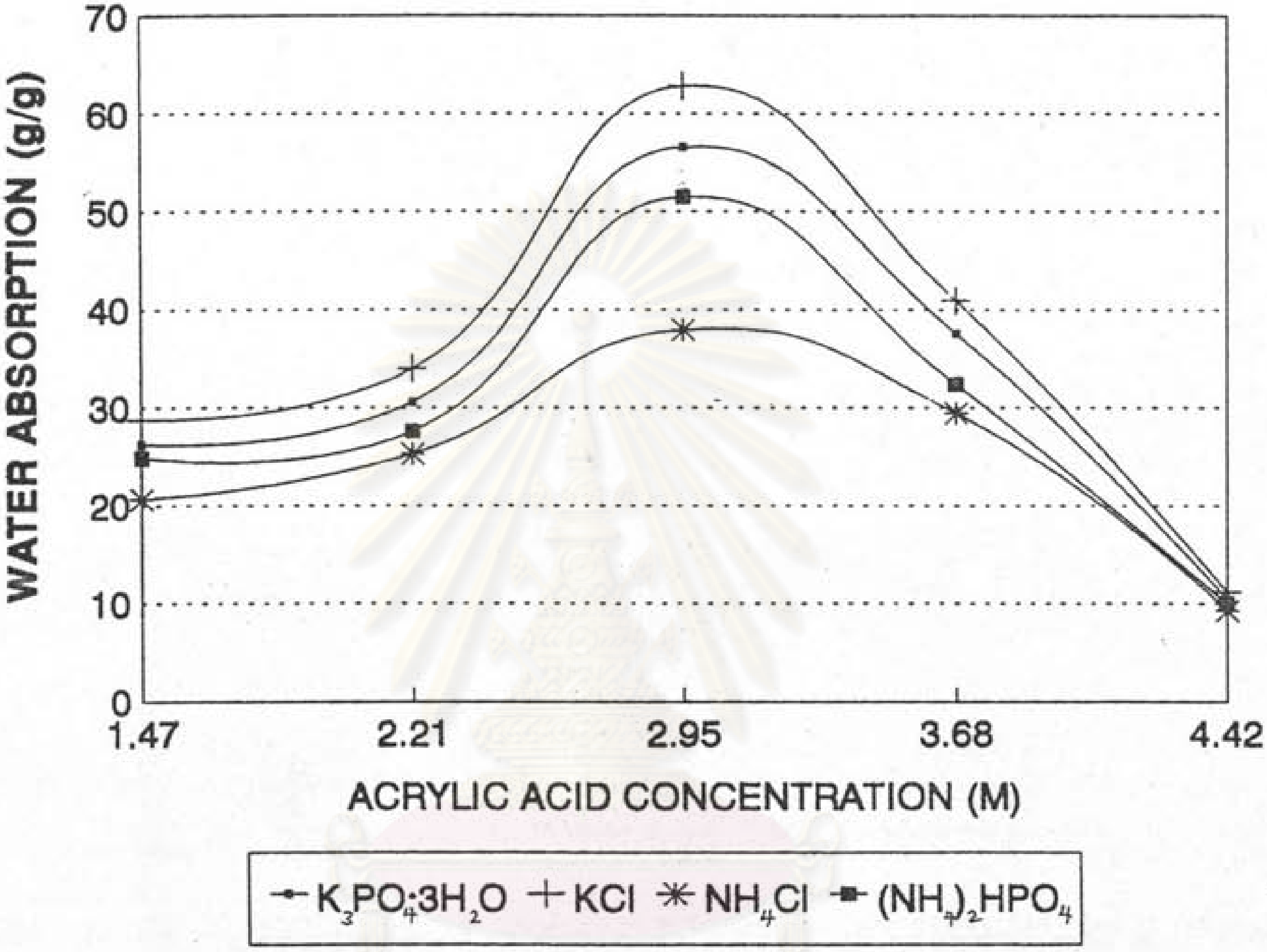

Figure 4.22 Effect of the concentration of acrylic acid on water absorption of saponified starch-g-poly(acrylic acid) copolymer in KCl, $K_3PO_4.3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ solutions of 0.9% w/w.

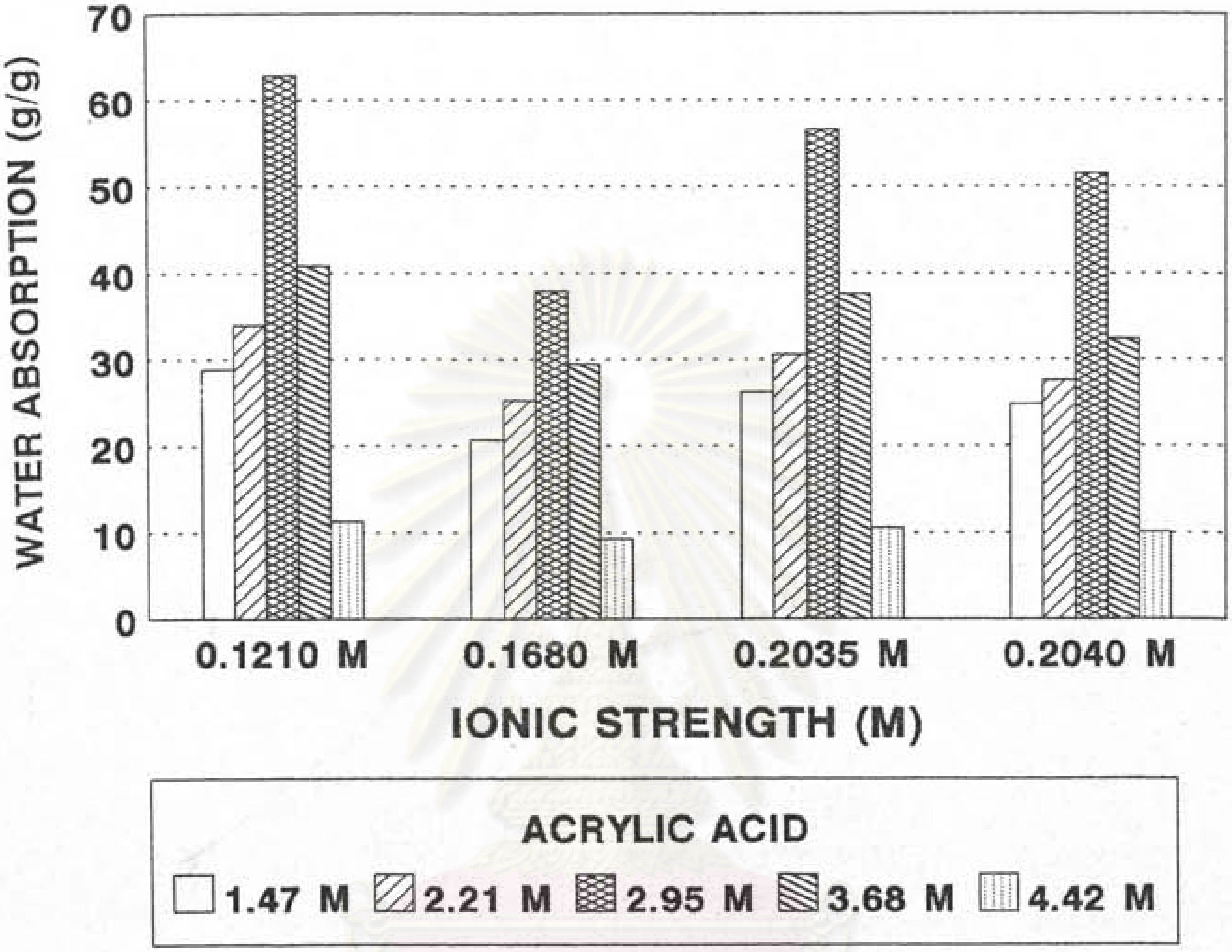

Figure 4.23 Effect of the ionic strengths of 0.9% w/v KCl, $K_3PO_4.3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ solutions on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various acrylic acid concentrations.

$$Q^{5/3} = \left[\left(\frac{i}{2.V_u S^{*1/2}} \right)^2 + (1/2 - x_1)/v_1 \right] (\nu_e/V_o) \quad (4.17)$$

where,

i : degree of ionization of polymer electrolyte

S^* : ionic strength of salt solution added

$(1/2 - x_1)/v_1$: affinity between ionic network and the absorbed water

v_u : molar volume of polymer repeating unit

ν_e/V_o : crosslinking density

Figure (4.25) shows the relationships between the absorbency (Q) and the factors mentioned above (84).

The different water absorption in the solution of salts depends on the effect of osmotic pressure as described in eq. (4.14), ionic strength of salt solution, and other factors described in eq. (4.17): crosslinking density, molar volume of polymer repeating unit and the affinity of the polymer network and the absorbed water.

4.6.2 Effect of Hydrogen Peroxide Concentration on Water Absorption.

The water absorption of the graft copolymer in the presence of $K_3PO_4.3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ is given in Table 4.11 and Figures 4.25-4.26. All of these salts have a concentration of 0.9% w/w as the previous section.

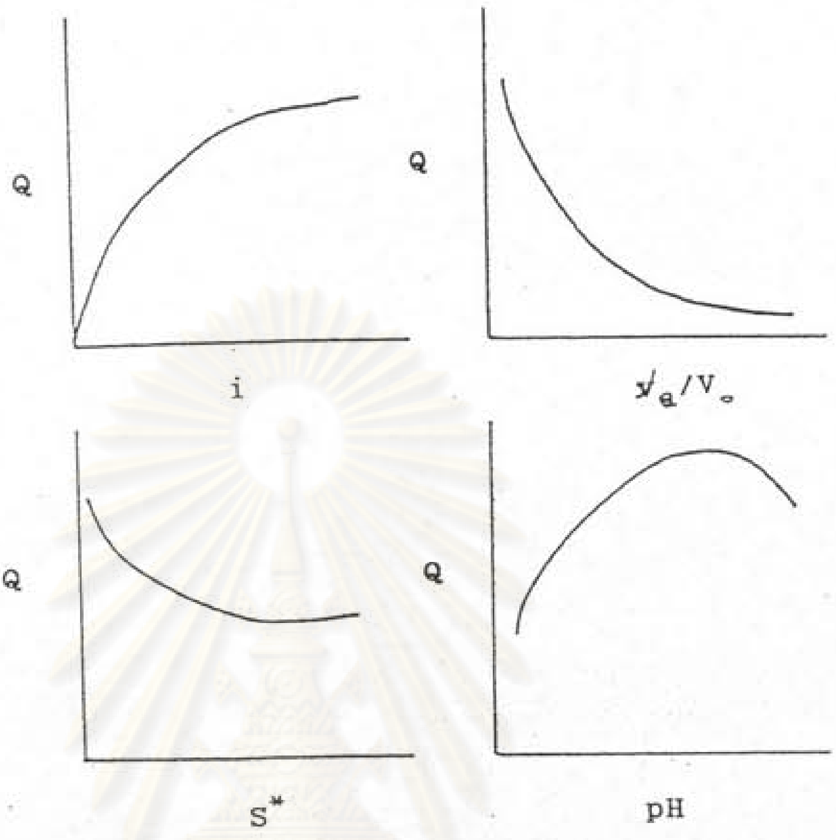

Figure 4.24 Relationships between Swelling Degree and Ionization Degree of Polymer Electrolyte, Crosslinking Density of Polymer Network, Ionic Strength of Salt Solution, and pH of Polymer Solution.

The experimental data show that the effect of 0.9% w/w of KCl, $K_3PO_4 \cdot 3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ dramatically decreases water absorption in the presence of ions. The higher ion concentration, the lesser water absorption. This phenomenon is best explained in terms of swelling of the modified starch containing anionic groups as described above in 4.6.1.

TABLE 4.11

Effect of the Hydrogen Peroxide Concentration on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymers in $K_3PO_4.3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ Solutions with an Identical Concentration of 0.9% w/w

Hydrogen peroxide concentration (M)	Water absorption in $K_3PO_4.3H_2O$[a] (g/g) (0.204)	Water absorption in KCl[b] (g/g) (0.121)	Water absorption in NH_4Cl[c] (g/g) (0.168)	Water absorption in $(NH_4)_2HPO_4$[d] (g/g) (0.204)
0.0553	13.0	14.4	8.7	11.7
0.1107	36.7	40.8	24.6	33.5
0.1661	46.3	51.2	30.9	42.1
0.2217	56.6	62.8	37.9	51.5
0.2768	9.5	10.5	6.4	8.6
0.3322	4.5	5.1	3.1	4.1

[a] $[K^+]=0.101$, $[PO_4^{-3}]=0.034$, $[K^+]+[PO_4^{-3}] = 0.135$ mole-ion/dm^3, ionic strength = 0.2035 M.

[b] $[K^+]=[Cl^-] = 0.121$, $[K^+]+[Cl^-] = 0.242$ mole-ion/dm^3, ionic strength = 0.1210 M.

[c] $[NH_4^+]=[Cl^-] = 0.168$, $[NH_4^+]+[Cl^-] = 0.336$ mole-ion/dm^3, ionic strength = 0.1680 M.

[d] $[NH_4^+]=0.136$, $[HPO_4^{-2}]=0.068$, $[NH_4^+]+[HPO_4^{-2}] = 0.204$ mole-ion/dm^3, ionic strength = 0.2040 M.

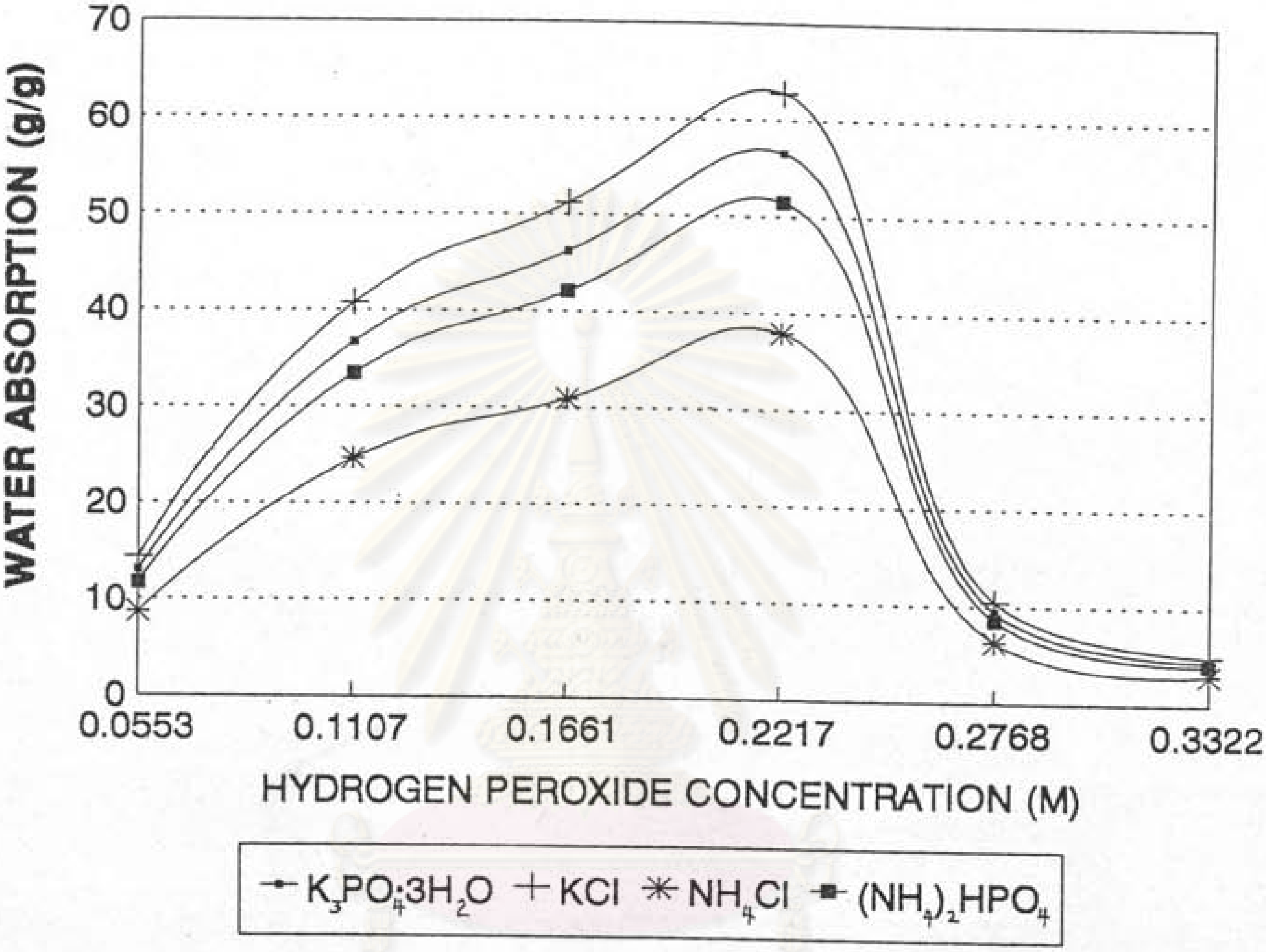

Figure 4.25 Effect of the concentration of hydrogen peroxide on water absorption of saponified starch-g-poly(acrylic acid) copolymer in KCl, $K_3PO_4.3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ solutions of 0.9% w/w.

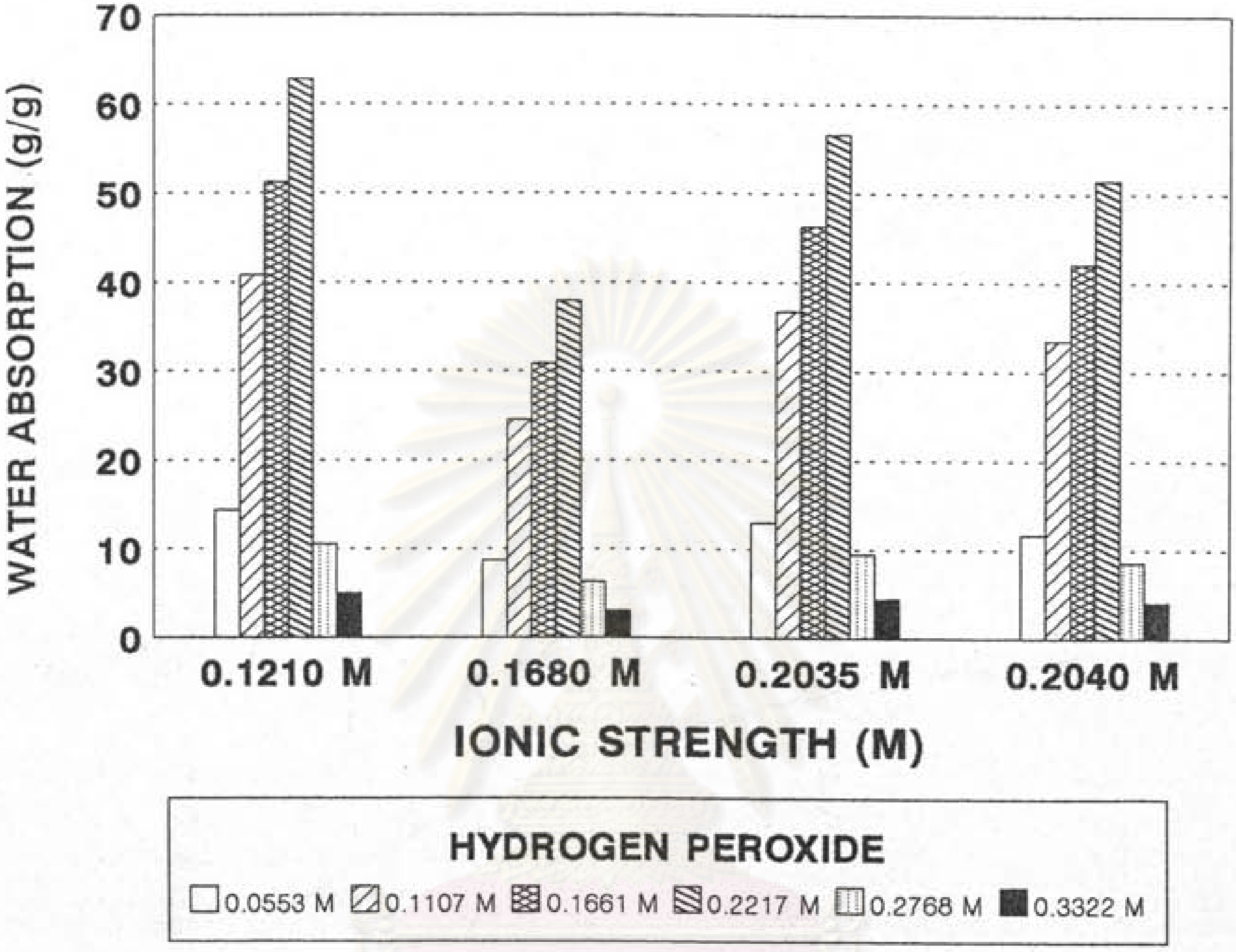

Figure 4.26 Effect of the ionic strengths of 0.9% w/v KCl, $K_3PO_4 \cdot 3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ solutions on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various hydrogen peroxide concentrations.

4.6.3 Effect of Reaction Temperature.

The water absorption of the graft copolymer in the presence of $K_3PO_4.3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ is given in Table 4.12 and Figures 4.27-4.28. All of these salts have a concentration of 0.9% w/w.

The experimental data show that the effect of 0.9% w/w of KCl, $K_3PO_4.3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ dramatically decreases water absorption. The higher the ion concentration, the lesser the water absorption. This phenomenon is best explained in terms of the swelling of modified starch containing anionic groups as described above in 4.6.1.

4.7. Water Absorption in Sand Alone and Sand with Saponified Starch-g-poly(acrylic acid) Copolymers.

In order to determine the water retention capacity in soil environment, the newly hydrolyzed satrch-g-poly (acrylic acid) copolymer was tested by mixing with sand having the particle size average of larger than 200 mesh at the concentrations of 0.5, 1.0, 2.0, and 3.0%. The absorption data are given in Table 4.13 and illustrated in Figure 4.29 and the absorption of sand alone is 0.3 g/g. They clearly show that the water retention in sand depends, to a large extent, on the amount of copolymer used. There is a linear relationship between water retention and polymer concentration, i.e. the concentration of the grafted

TABLE 4.12

Effect of the Reaction Temperature on Water Absorption of the Saponified Starch-g-poly(acrylic acid) Copolymers in $K_3PO_4.3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ Solutions with a Concentration of 0.9% w/w

Reaction temperature (°C)	Water absorption in $K_3PO_4.3H_2O$[a] (g/g) (0.204)	Water absorption in KCl[b] (g/g) (0.121)	Water absorption in NH_4Cl[c] (g/g) (0.168)	Water absorption in $(NH_4)_2HPO_4$[d] (g/g) (0.204)
35	56.6	62.8	37.9	51.5
45	32.6	36.1	21.9	29.7
55	24.3	26.8	16.3	22.1
65	20.7	22.9	13.9	18.8

[a] $[K^+]=0.101$, $[PO_4^{-3}]=0.034$, $[K^+]+[PO_4^{-3}] = 0.135$ mole-ion/dm^3, ionic strength = 0.2035 M.

[b] $[K^+]=[Cl^-] = 0.121$, $[K^+]+[Cl^-] = 0.242$ mole-ion/dm^3, ionic strength = 0.1210 M.

[c] $[NH_4^+]=[Cl^-]=0.168$, $[NH_4^+]+[Cl^-] = 0.336$ mole-ion/dm^3, ionic strength = 0.1680 M.

[d] $[NH_4^+]=0.136$, $[HPO_4^{-2}]=0.068$, $[NH_4^+]+[HPO_4^{-2}] = 0.204$ mole-ion/dm^3, ionic strength = 0.2040 M.

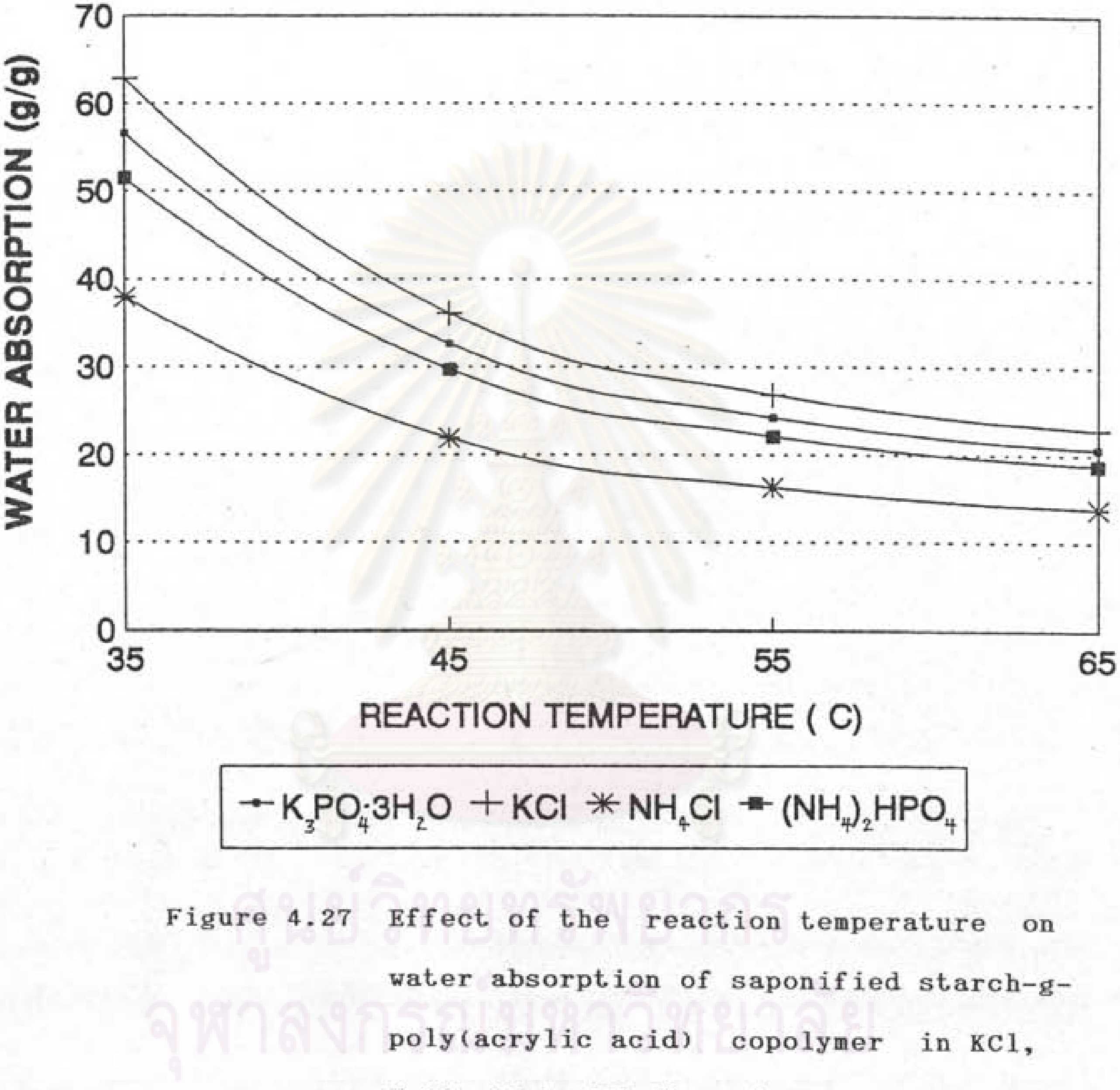

Figure 4.27 Effect of the reaction temperature on water absorption of saponified starch-g-poly(acrylic acid) copolymer in KCl, $K_3PO_4 \cdot 3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ solutions of 0.9% w/w.

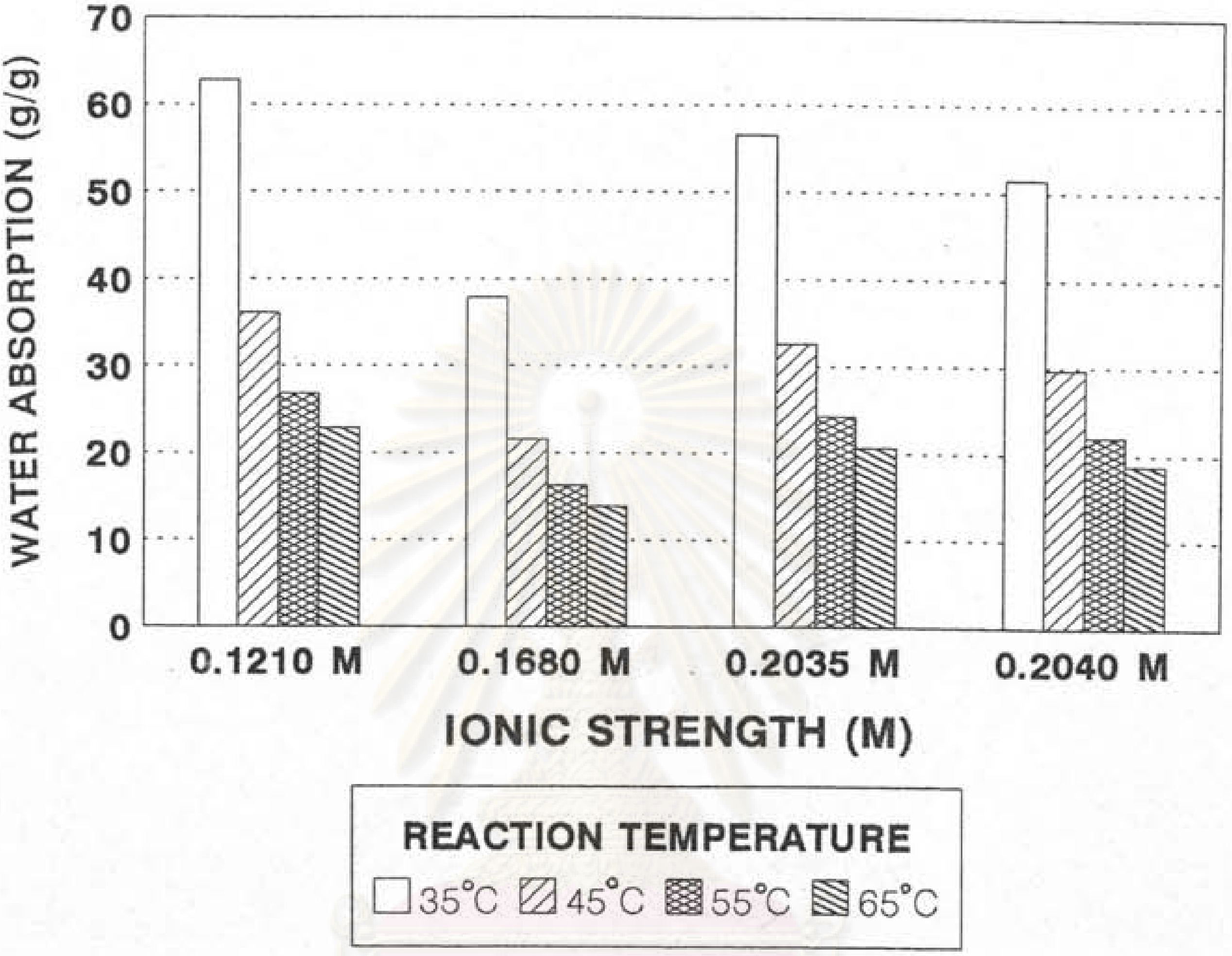

Figure 4.28 Effect of the ionic strengths of 0.9% w/v KCl, $K_3PO_4.3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ solutions on water absorption of the saponified starch-g-poly(acrylic acid) copolymers with various reaction temperatures.

copolymer increased, so did the water retention.

The water absorption efficiency of the copolymer also plays an important role in water absorption of sand. Indeed, as the starch(g)/Acrylic acid(M) ratio goes from 30:1.47, the water retention increases as well as those for 30:2.21, 30:2.95 ratios, then the water absorption decreases for 30:3.68 and 30:4.42 ratios. The water absorption pattern is almost identical as showed in Figure 4.30.

TABLE 4.13

Water Retention of Sand Mixed with Different Concentrations of Saponified Starch-g-Poly(acrylic acid) copolymers.

Starch(g) /Acrylic acid(M)	Water retention (g/g) by the addition of			
	0.5% polymer in sand	1.0% polymer in sand	2.0% polymer in sand	3.0% polymer in sand
30:1.47	37.63	38.49	39.25	43.84
30:2.21	44.92	48.89	51.19	54.89
30:2.95	123.37	128.58	132.43	141.08
30:3.68	78.66	82.25	84.54	91.81
30:4.42	18.78	19.64	21.29	21.94

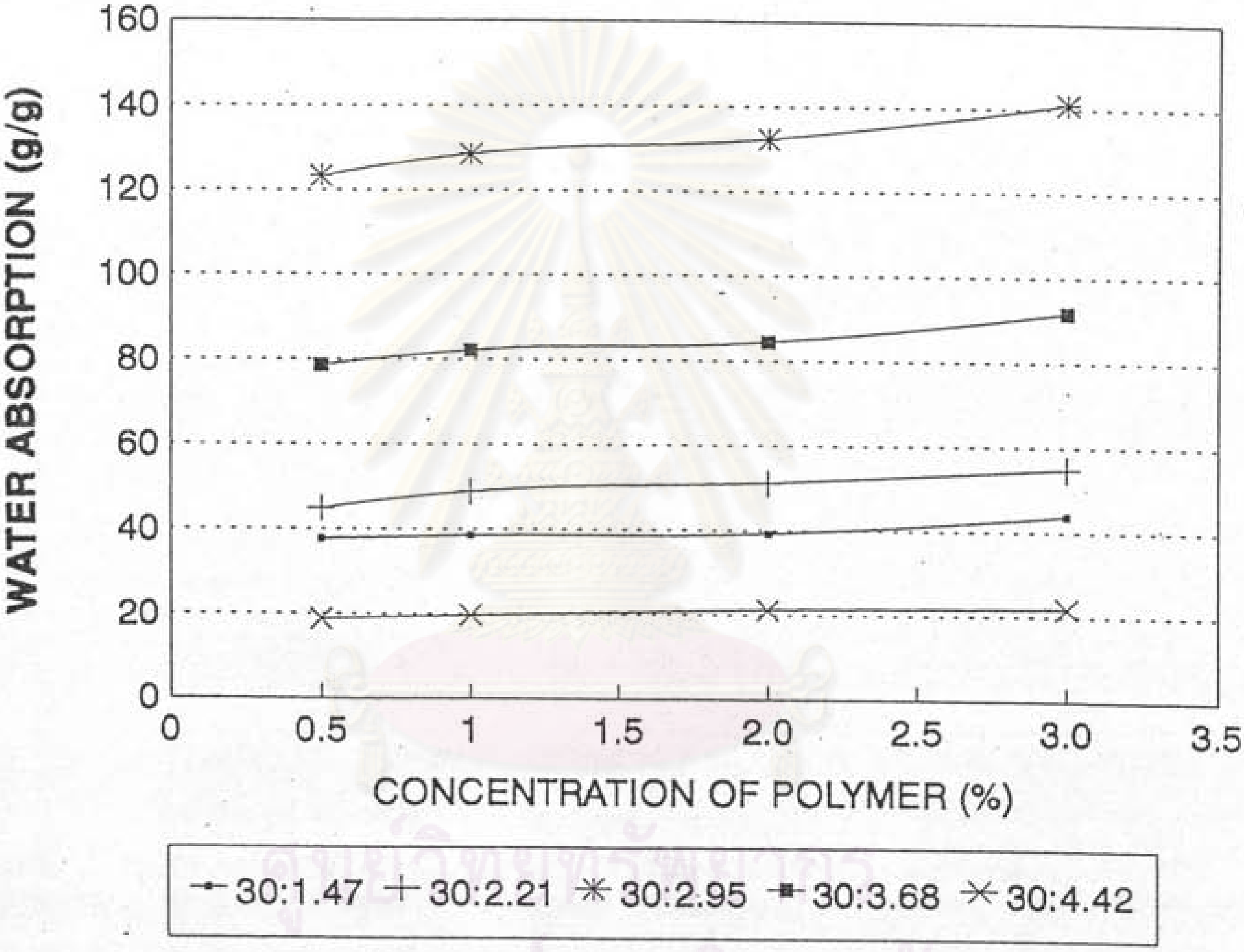

Figure 4.29 Water retention of sand mixed with different concentrations of the saponified starch-g-poly(acrylic acid) copolymers.

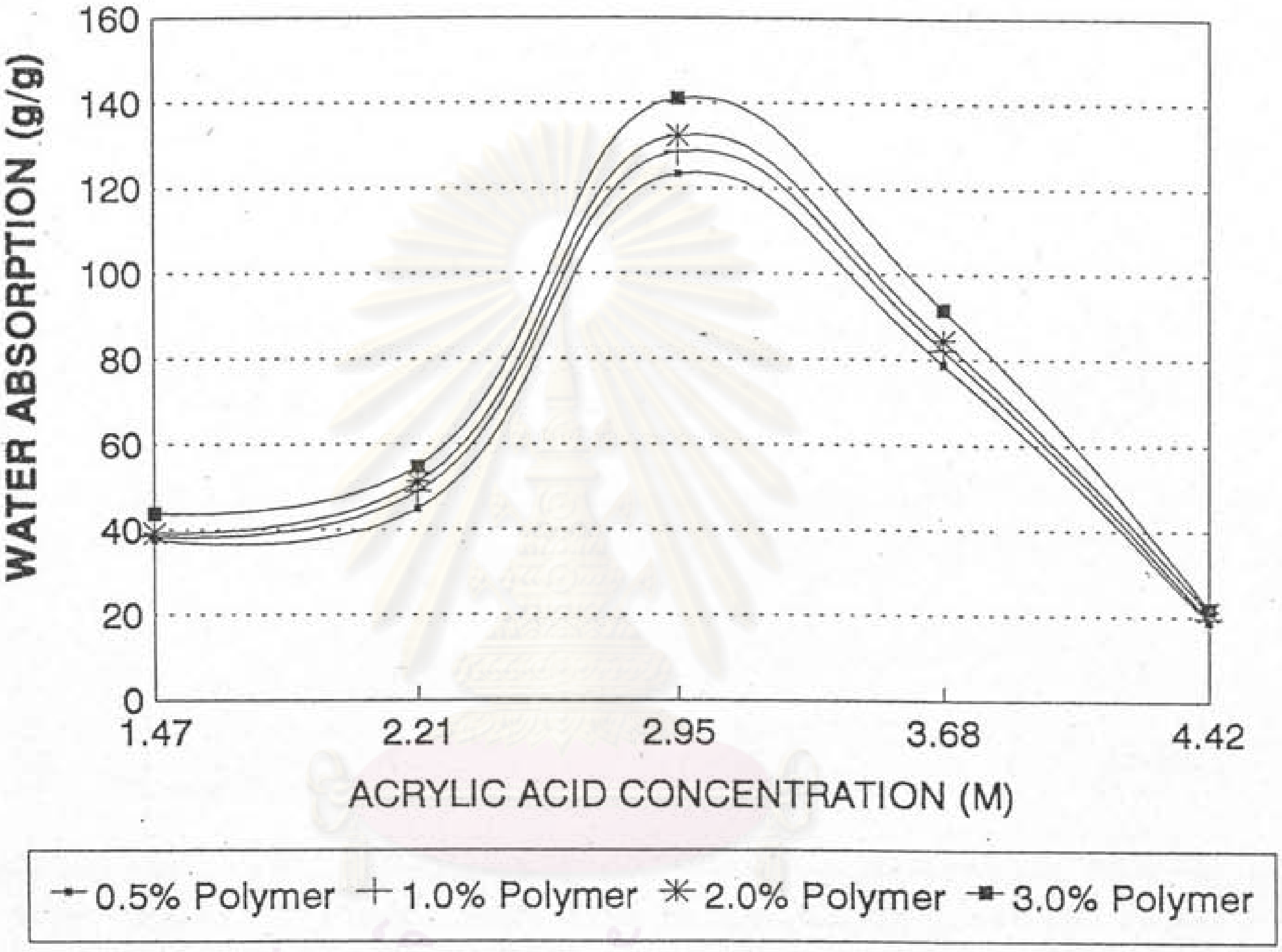

Figure 4.30 Water retention of sand mixed with different acrylic acid concentrations in the saponified starch-g-poly(acrylic acid) copolymers.