Rate of Swelling of Sodium Polyacrylate

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SYNOPSIS

The kinetics of the swelling of sodium polyacrylate (NaPA), a hydrophilic polymer, was studied gravimetrically, by microscopic observation, and calorimetrically. The swelling process followed first-order kinetics and the rate constant was of the order of 10^{-2} s^{-1}. The gravimetric method, however, was not useful for kinetic studies. The rate constant was depressed by the addition of sodium chloride. The activation energy of the swelling was 46.0 ± 6.2 (kJ mol^{-1}) and decreased with the increase in sodium chloride concentration. In acid solution, the activation energy was almost the same as that in water. The heat of the swelling was 196 ± 17 J g^{-1} and did not vary with the addition of sodium chloride. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Hydrophilic polymers, such as sodium polyacrylate, absorb a larger amount of water than do conventional water-absorbing materials, and the absorbed water is not removable even under some pressure. Because of these peculiar properties, hydrophilic polymers are used in many fields of sanitation, industry, and agriculture.[1,2]

The mechanism of absorption of water of hydrophilic polymers was explained in an ion-network structure theory by Flory[3]; however, detailed information on their kinetics has not been found, because the rate of the swelling is too rapid to study by normal methods.

In this paper, the kinetics of the swelling of sodium polyacrylate (NaPA) under several conditions was studied by picture analysis with a microscope–VTR system, calorimetrically and gravimetrically. The results are discussed on the swelling of NaPa from the viewpoint of the kinetics.

EXPERIMENTAL

Sodium polyacrylate powder was used with particles 100–250 μm in diameter, supplied by KAO Co. The magnifying power of water absorption is decreased under acid (below pH 6) or base (over pH 10) conditions.[4]

The tea-bag weight method, picture analysis, and calorimetrical analysis were used for the kinetics of the swelling of NaPA. With the tea-bag weight method, about 20 mg of NaPA was put in a tea bag of polyester nonwoven fabric and dipped into distilled water or solutions. After a passage of time, the tea bag was centrifuged by a hand-centrifuge as soon as possible, then weighed.

For the picture analysis, NaPA was set on a slide glass of a microscope (Nikon Microphoto-FX) connected to a VTR and distilled water or solutions were poured on the NaPA from a hypodermic needle. The volume changes of the NaPA were videotaped. By replay at low speed on the VTR, the changes of diameter of the NaPA were measured. The volume changes were calculated by the equation $V = 4/3\pi(d/2)^3$, where d is the diameter of NaPA on the video. The particles are assumed to be spherical.

For the calorimetric method, the heat of the swelling was measured with a twin isoperibol calorimeter (Tokyo Riko Model TIC-22). The schematic display of the calorimeter is shown in Figure 1. The symmetrical twin Dewar vessels are in an aluminum block that has a large thermal capacity. One of the cells is for the reference and contains water of the same weight as that of the sample, and the other is for the sample. After the system had reached thermal equilibrium, the sample was rapidly mixed into 70 mL of distilled water or solution by breaking the ampule.

Because the calorimeter is an adiabatic type, the heat of the swelling was calculated from the calibration curve of the standard heat. The time constant τ of the heat leak of the system was $1.37 \times 10^{-1}\,s^{-1}$.

RESULTS AND DISCUSSION

Changes of water absorption of NaPA and dependence of sodium chloride were measured by the tea-bag weight method. The results are shown in Figure 2. The magnifying power of the water absorption was about 200. This value was appreciably less than that reported in the literature.[4] The small value of absorption power may be due to the pH 5–6 of the distilled water. The power of water absorption was greatly decreased with 1% sodium chloride and did not change very much with increasing its concentration.

However, it was impossible to do kinetic analysis by this method, because the weight change for the water absorption was completed in about 1.5 min and measurements were possible no more frequently than at intervals of 20–30 s.

The water absorption and dependence of sodium chloride were measured by microscopic observation. Figure 3 shows the volume change of NaPA with water, and Figure 4 shows the change of ratio of volume at time t, V_t, and volume at time zero, V_0.

As shown in Figure 4, the final volume change for 0% sodium chloride was 280 times the initial volume using microscopic observation, but, gravi-
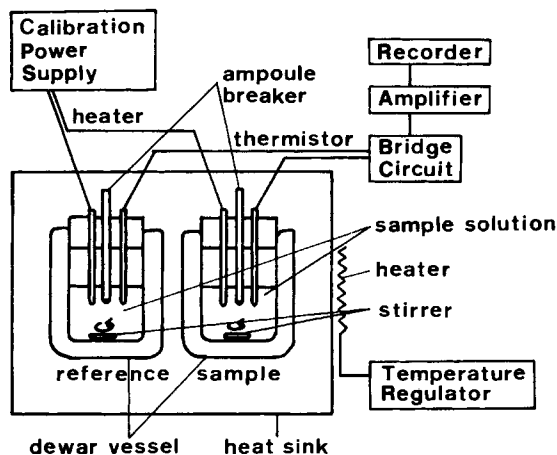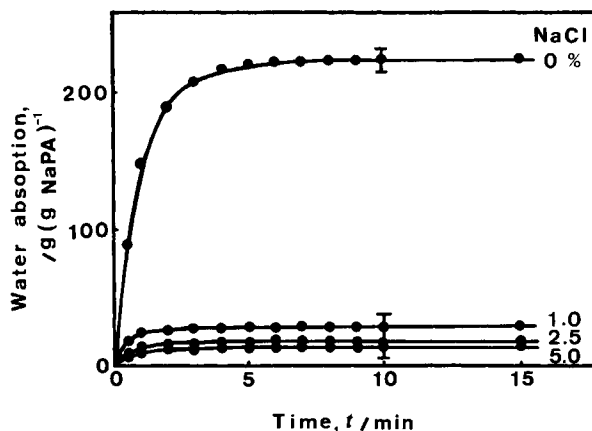

Figure 2 Effect of sodium chloride concentration on the time course of water absorption obtained by the tea-bag weight method at 25°C.

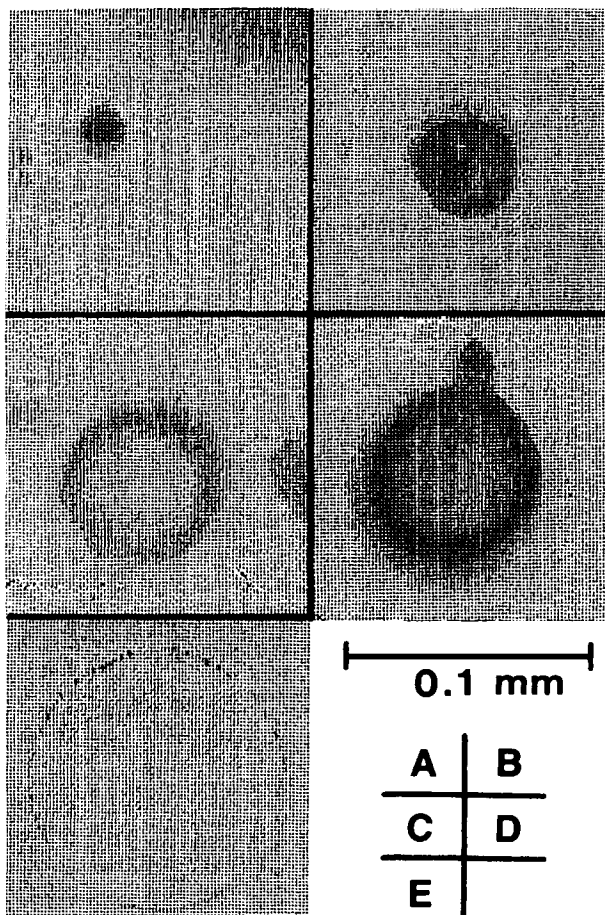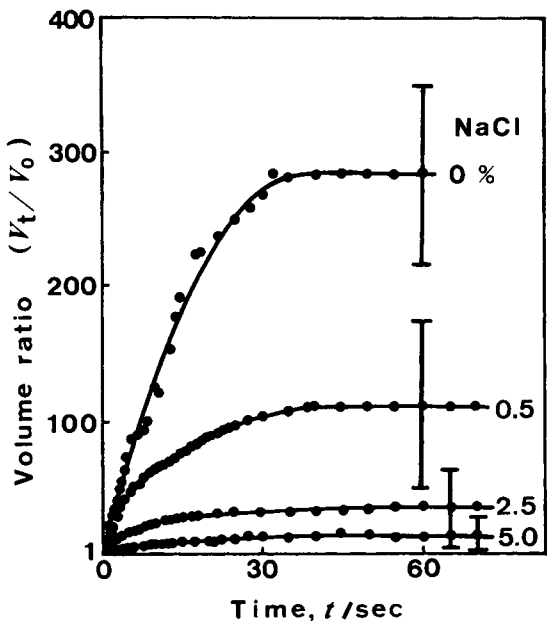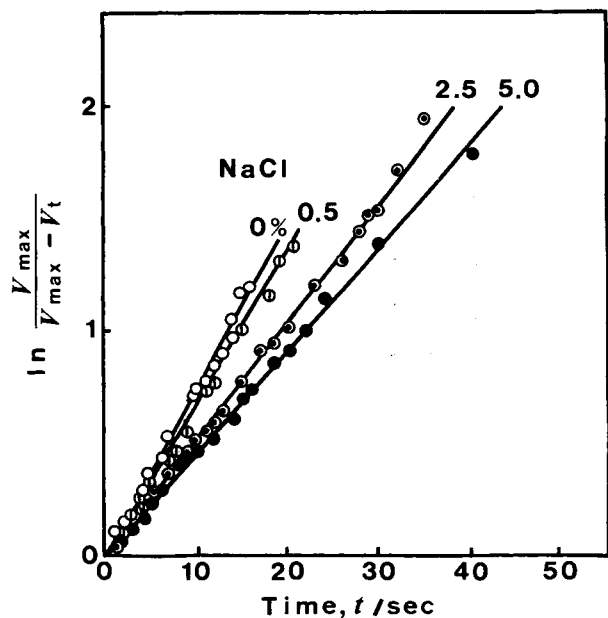**Figure 1** Schematic display of the isoperibol calorimeter.

Figure 3 Microscope graphs of water absorption of NaPA: (A) before addition of water; (B) 1 s after addition; (C) 5 s after addition; (D) 10 s after addition; (E) 45 s after addition.
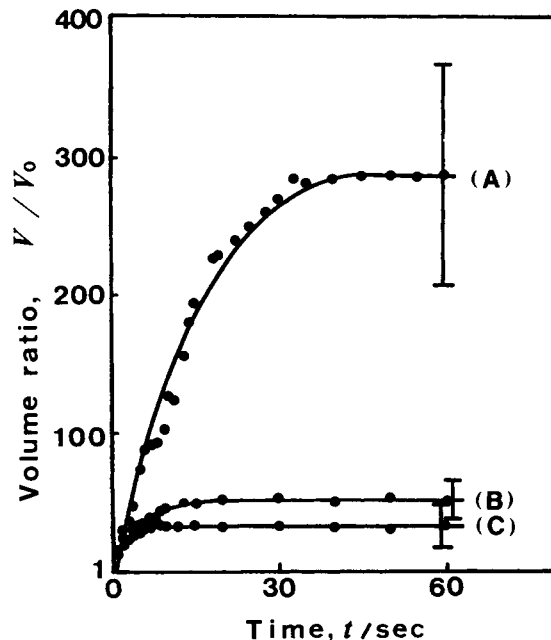
Figure 4 Effect of sodium chloride concentration on the time course of the volume ratio obtained by microscopic observation at 25°C.

metrically, the final water absorption was 210 times, as shown in Figure 2. The difference may be due to the removal of weakly bound water on the surface of NaPA by centrifugation.

By addition of sodium chloride, the maximum swelling volume, V_{max}, was depressed and the time

Figure 6 Effect of some acids on the time course of the volume ratio obtained by microscopic observation at 25°C: (A) water; (B) 0.1 N acetic acid; (C) 0.1 N lactic acid.

for equilibrium increased with its increasing concentration. Logarithms of volume changes were plotted against time. As illustrated in Figure 5, straight lines were obtained, showing that the volume change of the swelling of NaPA apparently fol-

Figure 5 Logarithmic plot of volume change vs. time obtained by microscopic observation at 25°C.
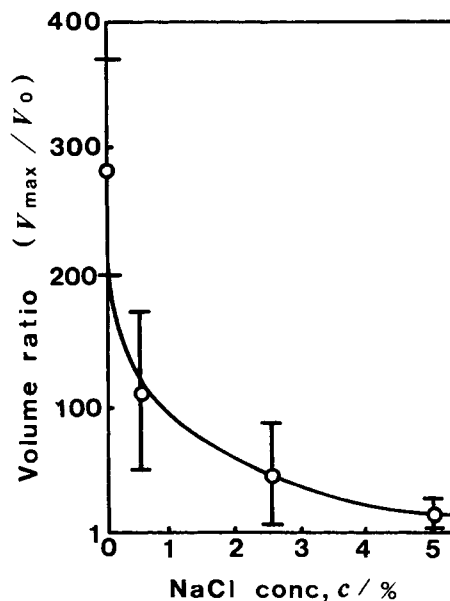
Figure 7 Effect of sodium chloride on the magnification of water absorption of NaPA obtained by the microscope method at 25°C.
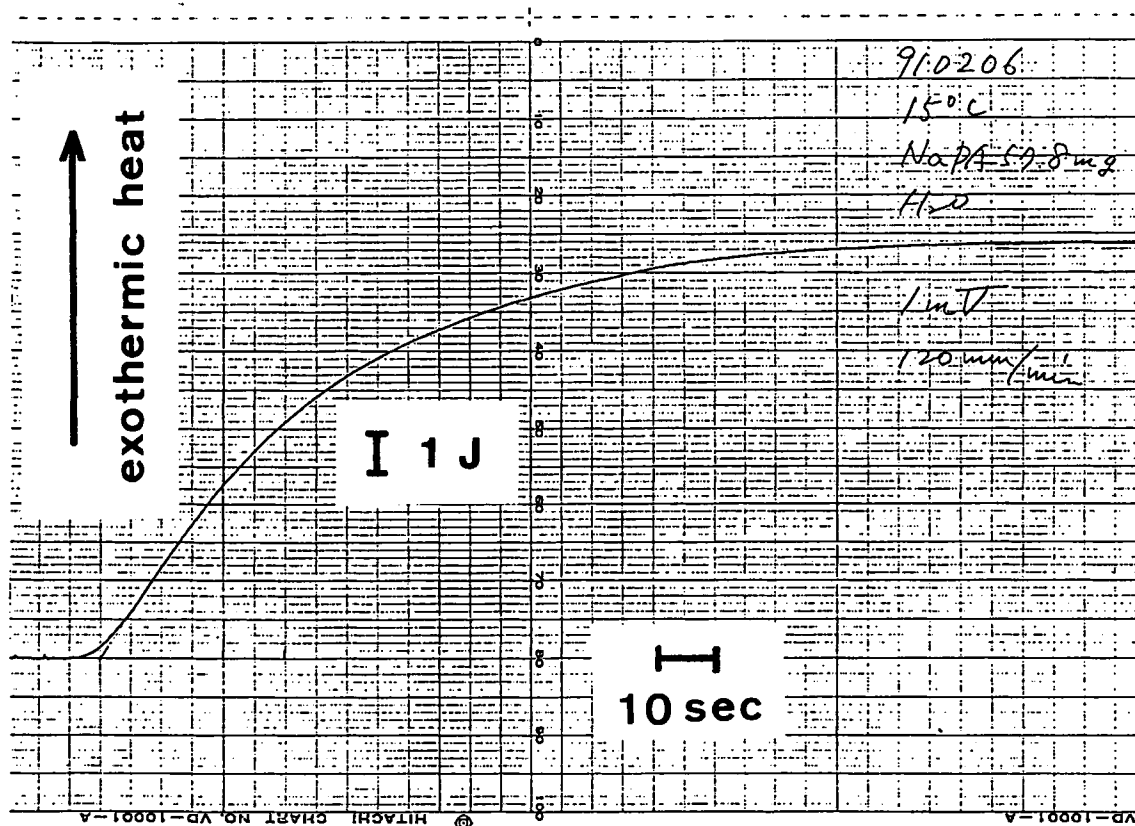
Figure 8 A typical calorimetric chart of water absorption of sodium polyacrylate.

lows first-order kinetics. Despite the rapid swelling reaction of NaPA, the volume could be measured every 1/30 s by microscopic observation, and we could follow the reaction fairly well. The value of V_0 varied, however, because of the difficulty in controlling the initial humidity.

The effect of acid on the swelling of NaPA was measured by microscopic observation, and these data are shown in Figure 6. The swelling volume was depressed to the same extent as was sodium chloride.

The ratios of V_{max} to V_0 were plotted as a function of the concentration of sodium chloride and are illustrated in Figure 7, showing that V_{max} was depressed with increasing sodium chloride concentration.

A typical thermogram of the swelling reaction of NaPA is shown in Figure 8 and the effects of sodium chloride on the heat of the swelling are shown in Figure 9. The swelling was exothermic and the heat of swelling of NaPA was 196 ± 17 J g^{-1}. The time to reach maximum heat was longer as the concentration of sodium chloride increased; however, the heat of swelling, Q_{max} did not depend on the concentration of sodium chloride.

To see the effect of sodium chloride on the rate

of swelling, the ratios of rate constants (k) of the swelling with various concentrations of sodium chloride to that with water (k_0) were plotted against the concentration of sodium chloride. As shown in Figure 10, at the lower concentrations of sodium
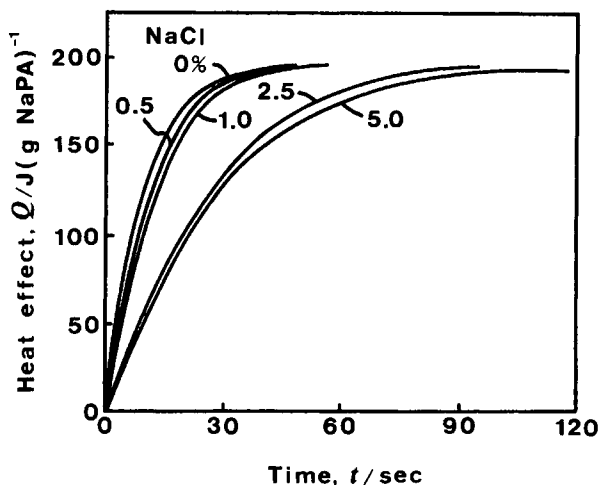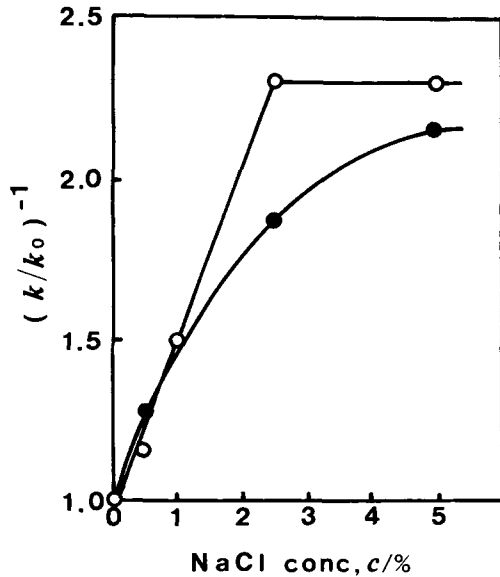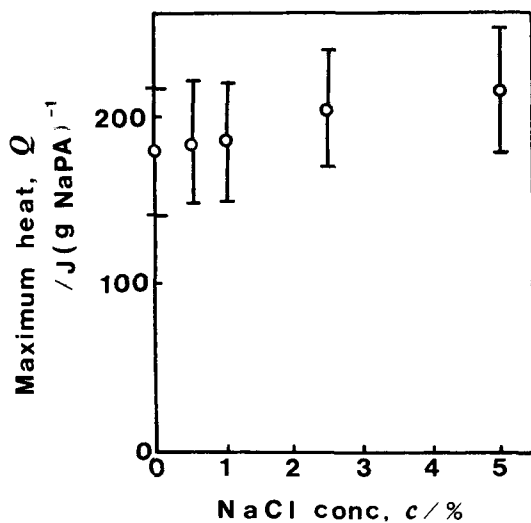

Time, t / sec

Figure 9 Effect of sodium chloride concentration on the time course of the heat effect obtained by calorimetry at 25°C.
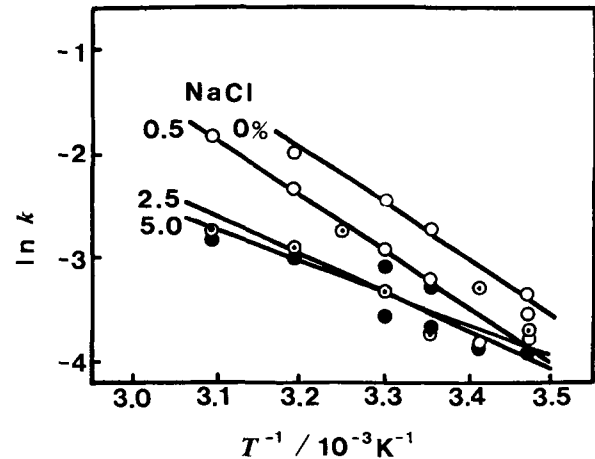
Figure 10 Reciprocal plot of the rate constant ratio vs. sodium chloride concentration at 25°C: (●) microscopic observation; (○) calorimetry.

Figure 12 Plots of ln k vs. the reciprocal of absolute temperature with sodium chloride concentration.

chloride, the ratios of the rate constants were almost the same by microscopic observation as by calorimetrical measurement, but at higher concentrations over 2.5%, the ratios were very different.

The effect of sodium chloride on the maximum heat of swelling is shown in Figure 11. The heat of swelling, Q_{max}, did not depend on sodium chloride and acid. These results differ greatly from the volume changes measured by microscopic observation, as shown in Figure 6.
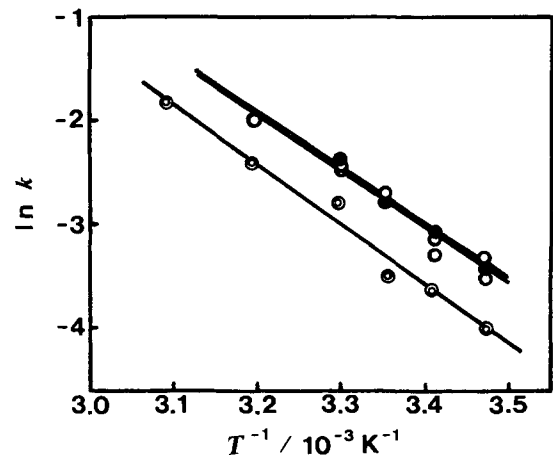
From the above results, it may be said that the heat of the swelling of NaPA reflects the same phenomena as does the weight change and the volume change at the initial stage. However, as swelling progresses, the heat of swelling becomes very small or nearly zero; that is, the heat behavior of the swelling reaction does not correlate with the gravimetric and the volume measurements.

Woessner et al.,[5,6] Aizawa et al.,[7,8] and Hatakeyama et al.[9] reported from NMR[5-8] and DSC[9] studies on agar,[5,6] Sephadex,[7,8] and poly(vinyl alcohol)[9] that there are three kinds of waters in gels of hydrophilic polymers and most of the water in gel is free water, which does not interact with polymers.

Figure 11 Relationship between maximum heat of water absorption and sodium chloride concentration.

Figure 13 Plots of ln k vs. reciprocal of absolute temperature with some acids: (○) water; (●) 0.1 N acetic acid; (◎) 0.1 N lactic acid.

From our present results, it is suggested that at the initial stage of swelling water may interact with NaPA and this interaction of water with NaPA is exothermic, because a hydrogen bond may be forming. The heat of swelling by free water following the interaction of water with NaPA may be nearly zero. Thus, it may be difficult to measure it calorimetrically. Figures 12 and 13 show Arrehenius plots of the rate constants of the swelling in solutions of sodium chloride and lactic and acetic acids that were obtained by calorimetric measurement. The slopes indicate the apparent activation energies of the swelling. These activation energies are listed in Table I.

As shown in Figure 12, the activation energy became smaller as the concentration of the salt increased. The results indicate that the thermostability increases with the increase in the concentration of the salt. The difference in osmotic pressure between internal and external gel will be smaller with increasing concentration of the salt. Therefore, it may be presumed that the three-dimensional spread of the gel will be depressed by the salt, and the depression might contribute to thermostability.

In contrast, as seen in Figure 13, the activation energies of the swelling in the solution of acetic and lactic acids were almost the same as the value for water, in spite of the fact that the degree of depression of the three-dimensional spread of the gel in the salt solution (2.5-5%) was the same as that in the acid solution (see Figs. 3 and 5).

In general, under acid conditions, the degree of dissociation of carboxyl groups decreases and the affinity for water should be reduced. Therefore, the gel would be more labile thermodynamically.

In acid solutions, the depression of three-dimensional spread should contribute to thermostability positively. On the other hand, decreasing of the dissociation of the carboxyl group might conduce to thermostability negatively, so that the value of the activation energy in acid solution might take almost the same order as that in water.

CONCLUSIONS

The kinetics of the swelling of sodium polyacrylate (NaPA) was studied gravimetrically, by microscopic

Table I   Activation Energy of Swelling of NaPA

Solution	E_A (kJ mol^{-1})
Water	46.0 ± 6.2
NaCl	
1.0%	45.2 ± 5.3
2.5	31.3 ± 10.5
5.0	26.1 ± 5.4
Acetic acid 0.1 N	48.6 ± 5.7
Lactic acid 0.1 N	45.8 ± 6.4

observation, and calorimetrically. The gravimetrical method was not useful for kinetical studies, because the rate of the swelling was too fast to follow the reaction. From the results obtained by microscopic observation and calorimetrically, it may be said that the swelling process apparently follows first-order kinetics and the rate constants are of the order of 10^{-2} s^{-1} and also that hydration of NaPA is prior to the penetration of free water into the gel of NaPA.

REFERENCES

1. F. Masuda, High Hydrophilic Polymer, Kyoritsu, Tokyo, 1990.
2. F. Masuda, Functional Mater., 4, 36 (1982).
3. P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953.
4. KAO Corp., K-6201 Technical Report, 1985.
5. D. E. Woessner, Jr., B. S. Snowden, and Y. C. Chiu, J. Colloid Interface Sci., 34, 283 (1970).
6. D. E. Woessner, Jr. and B. S. Snowden, J. Colloid Interface Sci., 34, 290 (1970).
7. M. Aizawa, J. Mizuguchi, S. Suzuki, S. Hayashi, T. Suzuki, N. Mitomo, and H. Toyama, Bull. Chem. Soc. Jpn., 45, 3031 (1972).
8. M. Aizawa and S. Suzuki, Bull. Chem. Soc. Jpn., 44, 2967 (1971).
9. T. Hatakeyama, A. Yamauchi, and H. Hatakeyama, Eur. Polym. J., 20, 61 (1984).