

# Effect of Concentration and pH of Solutions on the Absorbency of Polyacrylate Superabsorbents

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**ABSTRACT:** Polyacrylate superabsorbent (PAS) was synthesized by aqueous solution polymerization crosslinked by *N,N*-methylene bisacrylamide. The effect of pH and concentration of several solutions on absorbency ( $Q$ ) of PAS was studied. The results showed that the absorbency increased at first and then decreased with the increase of the solution's pH; the summit of the absorbing curve was attained when

pH was about 6.25. The relation between absorbency and pH could be represented by a quadratic equation and the square difference was relatively small. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 494–499, 2003

**Key words:** polyacrylate superabsorbent; absorbency; solution polymerization; pH

## INTRODUCTION

Superabsorbents can absorb a large amount of liquid and the absorbed liquid is hardly removable even under some pressure. They are applied in many fields, such as feminine napkins, disposable diapers, soil for agriculture and horticulture, water-blocking tapes, and drug delivery systems.<sup>1–4</sup>

Kiatkamjornwong and Phunchareon<sup>5</sup> studied the effect of pH on the swelling behavior of poly(acrylic acid-*co*-acrylamide) and concluded that the pH of external solutions had a profound effect on the balance of forces that determine equilibrium swelling in copolymers. Yao and Zhou<sup>6</sup> had also found that the absorbency of poly(acrylamide-sodium allylsulfonate-sodium acrylate) (poly(AM-SAS-AA)) in acid or base solution only increased from about 70 g g<sup>-1</sup> to 450 g g<sup>-1</sup> when pH was changed from 2 to 6, then the absorbency decreased to about 180 g g<sup>-1</sup> when pH was changed from 6 to 13. Lee et al.<sup>7,8</sup> studied the effect of pH on absorbency of poly(sodium acrylate-hydroxyethyl methacrylate) and concluded that the absorbency would not change greatly if the pH of solution was 2–14, which was accounted for the buffer action of the sodium carboxylate group with an acid or base. At the same time, they inferred that the absorbency showed a turning point when the pH of solution was about 6. The phenomenon reflected in their

articles probably showed something that was related to phase inversion.

This article mainly studied the effect of different pH of Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaHSO<sub>3</sub>, NaH<sub>2</sub>PO<sub>4</sub>–Na<sub>2</sub>HPO<sub>4</sub>, HCl, and NaOH solutions on absorbency of polyacrylate superabsorbent (PAS). The results showed that the absorbency of PAS varied with the change of the solution's pH. The relation between absorbency and pH could be expressed with different quadratic equations in different solutions. The explanation of the effect of pH on swelling behavior was also proposed from the structure of PAS.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) was distilled under reduced pressure and stored at 4°C until being used. *N,N*-methylene bisacrylamide (NMBA) and potassium persulfate (KPS) were used as received, all analytical grade and provided by Shanghai Chemical Reagent Factory (Shanghai, China). Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, NaHSO<sub>3</sub>, NaOH, HCl (aq), and NaCl were all analytical grade, supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China).

### Preparation of PAS

A mixture of acrylic acid and sodium acrylate was formed by slowly adding 36.5% NaOH to acrylic acid solution until the neutralization was 75%. The whole process was performed in an ice-water bath. Just before polymerization, NMBA used for crosslinker and KPS for initiator were added to the mixture. The re-

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action solution was put into a sealed glass tube, which was partly immersed in a water bath whose temperature was set to 40°C for 1 h, 60°C for 3 h, and 80°C for 1 h. When the polymerization was over, the product was taken from the reactor and cut into small pieces, then dried in an oven at 110°C overnight. Finally, PAS was pulverized into particles with the size no more than 160 mesh.

**Preparation of solutions with different pH**

Several solutions of NaHSO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>-NaH<sub>2</sub>PO<sub>4</sub>, NaOH, and HCl were prepared and each of them had several different concentrations. Then the pH of each solution was calculated according to their hydrolysis and/or ionization constants when the temperatures of all the solutions were 25°C, which would be introduced in theoretical analysis.

**Measurement of absorbency (25°C) in saline solutions**

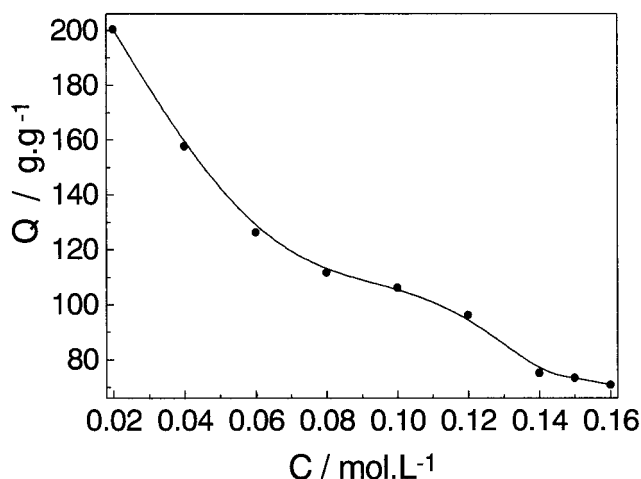
The accurately weighed PAS was immersed in each solution respectively for enough time so that the swelling equilibrium was attained. Then the unabsorbed liquid was screened with a 160 mesh nylon bag and the bag was weighed to determine the weight of liquid-swollen gel. The liquid absorbency (*Q*) was calculated using the following equation:  $Q = (W_2 - W_1)/W_1$ , where *W*<sub>2</sub> and *W*<sub>1</sub> are the mass of the liquid-swollen gel and the dry gel, respectively. *Q* was calculated as grams of liquid per gram of dry resin.

**Measurement of absorbing rate (25°C) in distilled water**

The accurately weighed PAS was simultaneously immersed in several glass cups full of distilled water with the temperature of 25°C, then the liquid-swollen gel in each glass cup was screened in an interval of every minute and the absorbency of PAS was determined according to the method mentioned above.

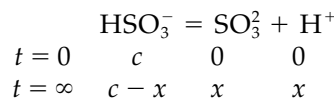
**Theoretical analysis**

For calculation of the pH of the four kinds of inorganic salt solutions, the method could be expressed as follows. Taking NaHSO<sub>3</sub> solution for example, HSO<sub>3</sub><sup>-</sup> had both hydrolysis and ionization. The hydrolysis constants of it (*K*<sub>h1</sub>) was 7.69 × 10<sup>-13</sup>, where *K*<sub>h1</sub> referred to the first-step hydrolysis of HSO<sub>3</sub><sup>-</sup> in solutions. The ionization constant of HSO<sub>3</sub><sup>-</sup> (*K*<sub>2</sub>) was 6.2 × 10<sup>-8</sup>. It was clear that *K*<sub>h1</sub> << *K*<sub>2</sub>, so there was



**Figure 1** Absorbency of PAS in NaCl solution with different concentrations.

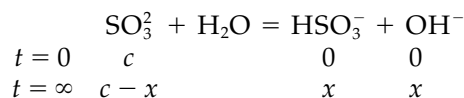
no necessity of thinking about the hydrolysis of HSO<sub>3</sub><sup>-</sup>. The ionization process of HSO<sub>3</sub><sup>-</sup> could be expressed as



where *c* referred to the initial concentration of NaHSO<sub>3</sub> solution. Thus, there was an equation of  $K_2 = x^2/(c - x) = 6.2 \times 10^{-8}$ , in which *x* and pH = -Lg[H<sup>+</sup>] could both be calculated.

In Na<sub>2</sub>SO<sub>4</sub> solution, [OH<sup>-</sup>] produced by the first-step hydrolysis of SO<sub>4</sub><sup>2-</sup> was much bigger than that produced by the second one because H<sub>2</sub>SO<sub>4</sub> was completely ionized for the first step and its constant for the second-step ionization was only 0.01. The method of calculating pH of solutions was the same as above.

Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were also inorganic salts that belonged to strong base/weak acid; two-step hydrolysis existed in their solutions. Taking the Na<sub>2</sub>SO<sub>3</sub> solution for example, the first-step hydrolysis constant of SO<sub>3</sub><sup>2-</sup> (*K*<sub>h1</sub>) and the second-step one (*K*<sub>h2</sub>) were 10<sup>-14</sup>/*K*<sub>2</sub> and 10<sup>-14</sup>/*K*<sub>1</sub>, respectively. Here *K*<sub>1</sub> and *K*<sub>2</sub> referred to the first- and second-step ionization constant of H<sub>2</sub>SO<sub>3</sub> in solutions, respectively. Because *K*<sub>1</sub> >> *K*<sub>2</sub>, *K*<sub>h2</sub> << *K*<sub>h1</sub>, which showed that the second-step hydrolysis of SO<sub>3</sub><sup>2-</sup> in Na<sub>2</sub>SO<sub>3</sub> solution could be omitted. The hydrolysis process could be expressed as follows:



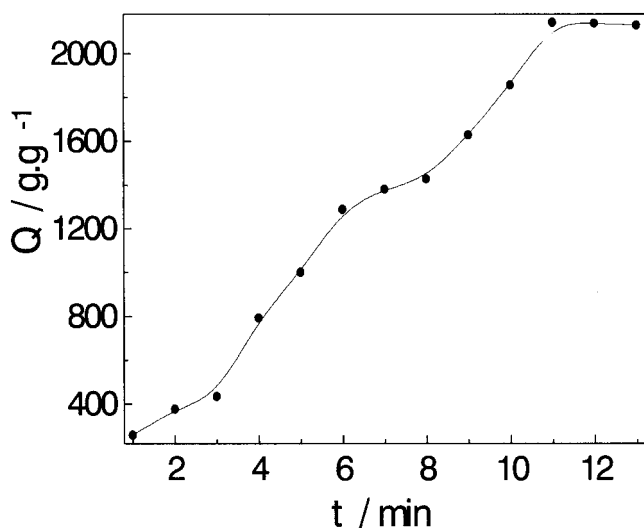


Figure 2 Absorbing rate of PAS in distilled water.

So there was such an equation as  $K_{h1} = x^2/(c - x) = 10^{-14}/K_2$ . Because  $K_2$  was constant when the temperature of solutions did not change,  $x$  could be calculated, which was also the concentration of  $\text{OH}^-$  in  $\text{Na}_2\text{SO}_3$  solution. Thus, the pH of  $\text{Na}_2\text{SO}_3$  solution could be calculated, too, as could the pH of  $\text{Na}_2\text{CO}_3$  solution.

## RESULTS AND DISCUSSION

### Fundamental properties of PAS

The absorbency of PAS in NaCl solutions with different concentration was proposed in Figure 1 when the temperature of solutions was 25°C. It showed that the water absorbency decreased with the increase of the solution's concentration. The absorbency in 0.9% NaCl solution was about 73  $\text{g g}^{-1}$  because the NaCl solution with the weight concentration of 0.9% was equal to the molar one of about 0.155  $\text{mol L}^{-1}$ .

The absorbing rate of PAS in distilled water was proposed in Figure 2 when the temperature of the water was kept at 25°C. The results showed that the rate was fast because the absorbency increased from 0 to 400  $\text{g g}^{-1}$  in 2 min and the equilibrium absorbency

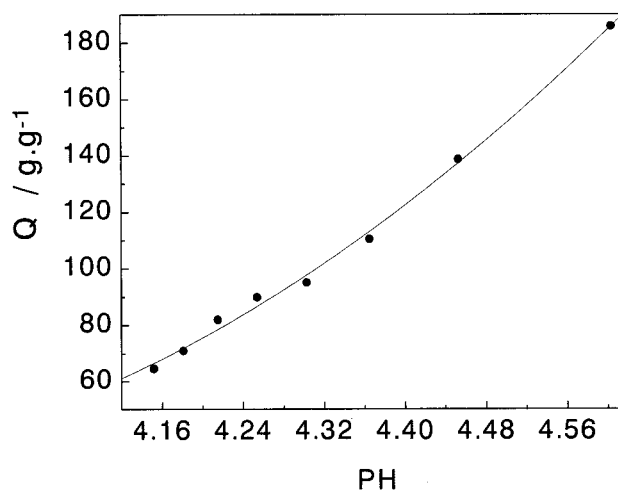


Figure 3 Absorbency of PAS in  $\text{NaHSO}_3$  solution.

of PAS was 2,143  $\text{g g}^{-1}$  when the absorbency did not increase any more 11 min later.

### Absorbency of PAS in solutions with different pH

Table I gives the results for absorbency ( $Q$ ) of PAS and the concentrations ( $C$ ) of  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{SO}_3$  solutions. It showed that absorbency decreased with the increase of the solution's concentration. Furthermore, if the absorbency of PAS was compared in  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$ , and  $\text{Na}_2\text{CO}_3$  solutions with the same concentration, it could be found that the absorbency was the highest in  $\text{Na}_2\text{CO}_3$  solution and the lowest in  $\text{Na}_2\text{SO}_4$  solution. This phenomenon could be qualitatively explained from the viewpoint of ionic radius and hydration of ion.<sup>9</sup> In the mixture of water and inorganic salt, water used as a very common ligand was likely to form hydrated ion with  $X^-$ , where  $X$  stood for  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ , and  $\text{CO}_3^{2-}$ . The bigger the ionic radius was, the stronger the tendency of hydration, so it could be concluded that  $\text{SO}_4^{2-}$  had the strongest capacity of hydration and  $\text{CO}_3^{2-}$  the weakest. At the same time, the attraction between  $\text{Na}^+$  and  $X^-$  was in the order of  $\text{SO}_4^{2-} < \text{SO}_3^{2-} < \text{CO}_3^{2-}$ , both of which led to the fact that the concentration of  $\text{Na}^+$  in  $\text{Na}_2\text{SO}_4$  solution was the biggest, whereas it was the smallest in  $\text{Na}_2\text{CO}_3$  solution.

TABLE I  
Absorbency (25°C) of PAS in  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$ , and  $\text{Na}_2\text{CO}_3$  Solutions with Different Concentrations

Solution	Concentration ( $\text{mol L}^{-1}$ )							
	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08
$\text{Na}_2\text{SO}_4$	130.88	104.98	97.86	79.15	70.99	60.37	58.46	56.88
$\text{Na}_2\text{SO}_3$	135.46	123.76	105.04	102.05	90.10	74.89	69.05	57.72
$\text{Na}_2\text{CO}_3$	191.12	134.84	126.65	110.41	100.07	94.07	77.91	70.84

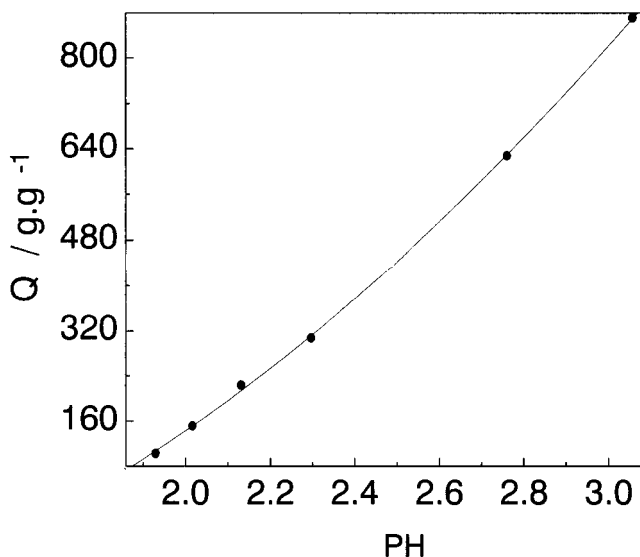


Figure 4 Absorbency of PAS in HCl solution.

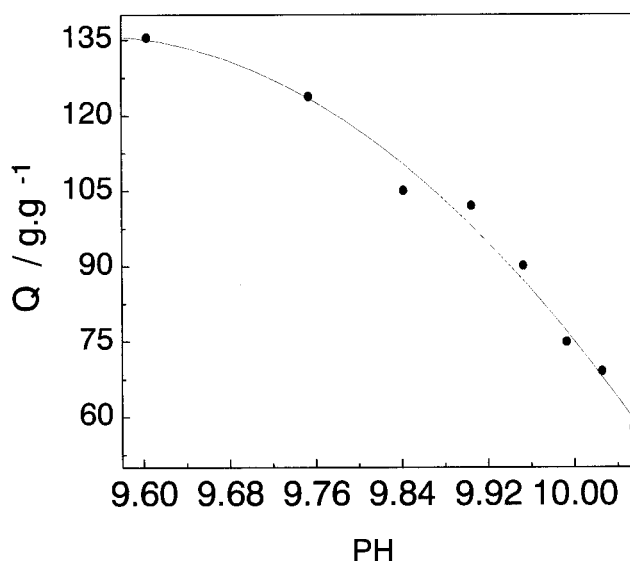


Figure 6 Absorbency of PAS in Na<sub>2</sub>SO<sub>3</sub> solution.

With this knowledge of the mechanism of absorbing water, we could infer that the difference of osmotic pressure between the structure of PAS and the outside solution was the key that made PAS able to absorb water. Besides, the osmotic pressure decreased with an increase of concentration of the outside salt solution. Therefore, as mentioned above, PAS had the smallest absorbency in Na<sub>2</sub>SO<sub>4</sub> solution and the biggest one in Na<sub>2</sub>CO<sub>3</sub> solution.

According to the above-mentioned method of calculating pH, the relation between Q and pH could be expressed as follows. Figure 3 gave the swelling behavior of PAS in NaHSO<sub>3</sub> solutions. It showed that the absorbency increased with the increase of pH when the range of pH in NaHSO<sub>3</sub> solution was from 4.1 to 4.7. This relation could be expressed by

$Q = A_1 + B_1pH + C_1pH^2$  with the square difference (SD) being 2.927, where  $A_1$ ,  $B_1$ , and  $C_1$  were all constants. The explanation of this trend was that the group of COOH began to ionize when PAS was soaked in solutions with its pH fitting for such relation as  $pH > pK_a$  (where  $K_a$  was the ionization constant of polyacrylate, which included the group of COOH). Both the number of COO<sup>-</sup> and the electrostatic distraction force became bigger, which made the network space of crosslinked polymer bigger also; as a result, the absorbency of superabsorbent increased. In order to verify this, several HCl solutions with different pH were made and the absorbency of PAS in these solutions were measured. The result was shown in Figure 4, which showed that the absorbency of PAS increased with the increase of the solutions' pH and the relation

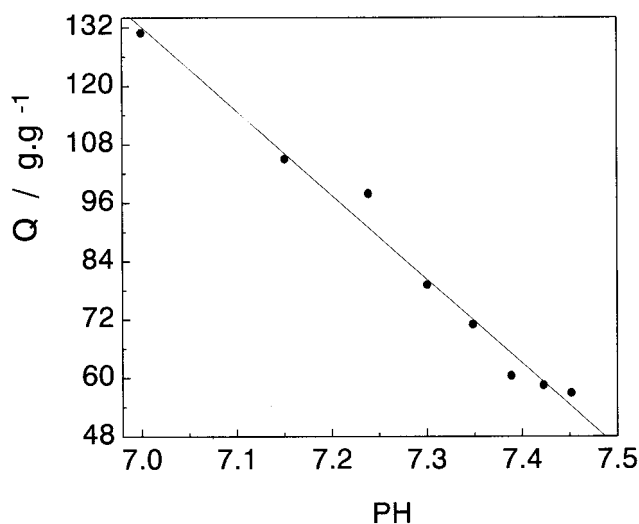


Figure 5 Absorbency of PAS in Na<sub>2</sub>SO<sub>4</sub> solution.

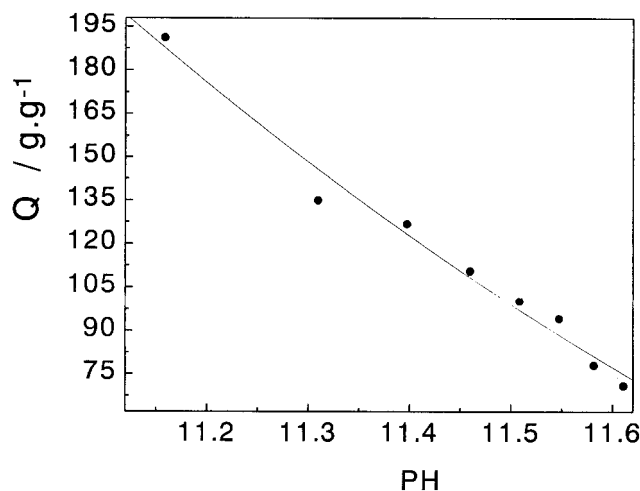


Figure 7 Absorbency of PAS in Na<sub>2</sub>CO<sub>3</sub> solution.

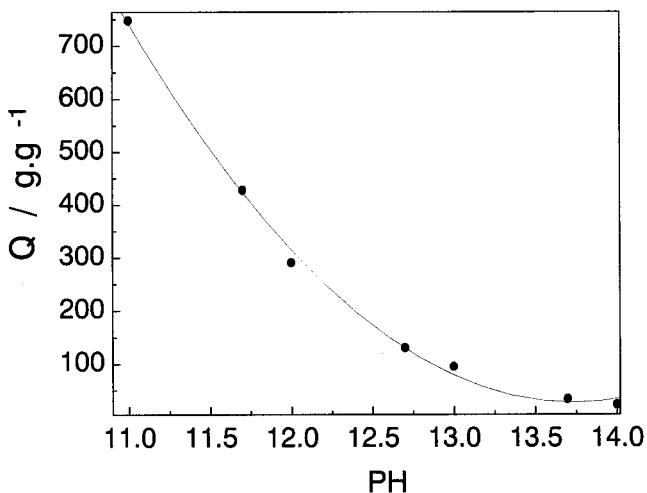


Figure 8 Absorbency of PAS in NaOH solution.

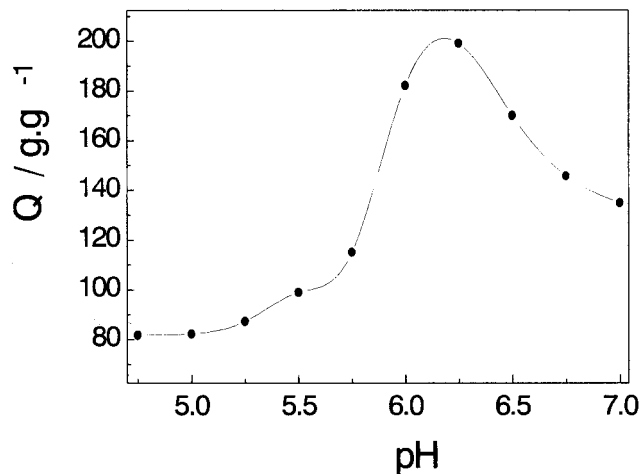


Figure 9 Absorbency of PAS in Na<sub>2</sub>HPO<sub>4</sub>-NaH<sub>2</sub>PO<sub>4</sub> solution.

between  $Q$  and pH could also be expressed as  $Q = A_2 + B_2\text{pH} + C_2\text{pH}^2$  when the pH was between 1.8 and 3.2.

With the increase of the pH of solution, there were some new changes for the swelling behavior of PAS, as shown in Figure 5, when it was immersed in Na<sub>2</sub>SO<sub>4</sub> solution whose pH was about 7. It showed that the absorbency decreased with the increase of solution's pH, and that the relation between  $Q$  and pH could be expressed by  $Q = A_3 - B_3\text{pH}$ ; the SD for this equation was 3.714.

Figures 6 and 7 expressed the relation between absorbency and pH in Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions. The experimental data in these two figures had good fit to the equation  $Q = A_i + B_i\text{pH} + C_i\text{pH}^2$  ( $i = 4, 5$ ) and the SD were 3.493 and 6.555, respectively. The two figures showed that the absorbency decreased with the increase of pH, which was contradictory to the plots shown in Figures 3 and 4. To demonstrate this, the absorbency of PAS in some NaOH solutions with different pH was measured as shown in Figure 8. It showed that the absorbency decreased with the increase of pH and that the relation between absorbency and pH conformed to the equation  $Q = A_6 + B_6\text{pH} + C_6\text{pH}^2$ , similar to the one shown in Figures 6 and 7.

The phenomenon could be explained as follows. When pH was much bigger than pKa, the concen-

tration of solutions was relatively high, and the ionic strength was high, too, which made it possible that the screening effect coming from the outside solutions became much stronger. Consequently, the number of anion on the chain of the polymer became small, which made the electrostatic distraction force and the elastic force weaker. Thus, the network of polymer shrank and the absorbency decreased.

In a word, whether the pH of saline solutions was equal to 7 or not, the swelling behavior of PAS could be represented by  $Q = A_n + B_n\text{pH} + C_n\text{pH}^2$  ( $n = 1-6$ ), where  $A_n$ ,  $B_n$ , and  $C_n$  were constants listed in Table II. The absorbency would not considerably change with the change of pH in solutions. The reason that could probably explain this phenomenon must resort to the fact that the groups of COOH and COONa existed in the chain of polymer at the same time, which had buffer action and was helpful in keeping the relative stability of absorbency for polymers even though the outside solution's pH changed. On the other hand, the relation between  $Q$  and pH showed that the absorbency increased with the increase of the solution's pH, as shown in Figures 3 and 4, with the range of pH from 1.8 to 4.7, then decreased with the increase of solution's pH, as shown in Figure 5-8, with the range of pH from 6.9 to 14. So there must be a range of pH during which the absorbency was the biggest. Figure 9

TABLE II  
Parameters A, B, and C in  $Q = A_n + B_n\text{pH} + C_n\text{pH}^2$  for the Absorbency (25°C) of PAS in Some Solutions

$n$	Solutions	Range of pH	A	B	C	SD	R <sup>2</sup>
2	HCl (aq)	1.8-3.2	-260.45	-116.17	158.9	6.829	0.9997
1	NaHSO <sub>3</sub>	4.1-4.7	2607.6	-1401.9	190.2	2.927	0.9962
3	Na <sub>2</sub> SO <sub>4</sub>	6.9-7.5	1340.5	-172.62	0	3.714	0.9916
4	Na <sub>2</sub> SO <sub>3</sub>	9.5-10.1	-27249	5735.1	-300.3	3.493	0.9881
5	Na <sub>2</sub> CO <sub>3</sub>	11.0-11.7	15413	-2436.2	96.05	6.555	0.9792
6	NaOH	11-14	18072	-2627.6	95.65	16.227	0.9975

was the swelling behavior of PAS in  $\text{Na}_2\text{HPO}_4$ - $\text{NaH}_2\text{PO}_4$  buffer solutions with different pH, which showed that the summit of absorbing curve was attained when the pH was about 6.25.

### CONCLUSIONS

The swelling behavior of PAS was related to the nature of external solutions. Both the concentration of solutions and the radius of anion were factors that influenced the absorbency of PAS. Furthermore, the relation between absorbency of PAS and pH of solutions could be expressed by a quadratic equation  $Q = A_n + B_n\text{pH} + C_n\text{pH}^2$  with different parameters for

different solutions whether the pH was equal to, less than, or more than 7.

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