Swelling Behaviors of Polyacrylate Superabsorbent in the Mixtures of Water and Hydrophilic Solvents

JUNWU CHEN, JIARUI SHEN

Department of Polymer Materials Science & Engineering, South China University of Technology, Guangzhou, Guangdong 510641, China

ABSTRACT: The swelling behaviors of polyacrylate superabsorbent in the mixtures of water and hydrophilic solvents, including methanol, ethanol, ethylene glycol, glycerol, acetone, dimethyl formamide, and dimethyl sulfoxide, were investigated. In 20 wt % solvent–water mixture, the superabsorbent with granularity between 40- and 80-mesh could reach swelling equilibrium at 25°C in several hours. It was also found that mixture temperature between 15 and 35°C had little influence on absorbency. Furthermore, the influence of water temperature between 0.5 and 99°C on absorbency was also rather limited when the superabsorbent was swelled by distilled water. The mixture concentration influenced absorbency significantly by changing the solubility parameter of the solvent–water mixture, particularly when the solubility parameter of the solvent–water mixture was < 20. The equilibrium absorbency was very high when the solubility parameter of the mixture was > 20, whereas the absorbing capacity of the superabsorbent was very low when the solubility parameter was < 17.5. The polarity fraction of solvents did not have any obvious influence on equilibrium absorbency, but not enough polarity fraction might affect the absorbing rate. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1331–1338, 2000

Key words: polyacrylate superabsorbent; swelling behavior; hydrophilic solvent; solvent–water mixture; solubility parameter

INTRODUCTION

Superabsorbent polymers are loosely crosslinked networks that can absorb a large amount of water in a short time and retain water under pressure. Therefore, superabsorbent polymers have great advantages over traditional water-absorbing materials such as cotton, pulp, sponge, etc. Superabsorbents are widely used in sanitary goods such as disposable diapers and hygienic napkins. They are also found to be valuable in some specialized applications, including artificial snow,[1,2] agriculture,[3–5] horticulture,[3,6] drilling fluid additives,[7]

polymer concrete suited for use in repairing cracks,[8] dew-preventing coating,[9] firefighting,[10] sealing composites in long-distance cable,[11,12] and drug delivery.[13,14]

The swelling of superabsorbents in water and its salt solutions was often reported to reveal their absorbing capacity.[15–17] However, studies of the swelling of superabsorbents in the mixtures of water and organic solvents are scarce. It is necessary to know the absorbency of superabsorbents in organic solvents where superabsorbents are concerned as assistants in fighting fire of organic solvent. It is also possible that superabsorbents are used to absorb the leaked mixtures comprised of water and solvents.

Murase and Fujita[18] reported on the swelling of superabsorbent in alcohol (methanol, ethanol,

isopropanol, glycerol)–water mixtures; however, only 20 and 50% concentrations were investigated. Recently, the absorbency of superabsorbent to methanol–water and ethanol–water mixtures within 0.5 h was reported by Liu and Rempel.[19]

Superabsorbent has the greatest absorbency in water. The addition of inorganic salt or organic solvent will decrease the absorbency. The solubility parameter (δ) of water is 23.2 and is the largest among the common solvents for polymers.[20] The polarity fraction (P) for water is also very high and its value is 0.819.[20] To study the swelling behaviors, including high solvent concentration, mutual solubility of the solvent to water is the first factor to be concerned within choosing solvents in the swelling study. The second factor is the wide δ range for the solvents. Seven hydrophilic organic solvents were used in this study, including four alcohols with small P [methanol, ethanol, ethylene glycol (EG), and glycerol] and solvents with high P [acetone, dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO)].[20] Among the seven solvents, the smallest δ is acetone; the smallest P is ethanol, and the solvent with the largest δ which is closest to that of water is glycerol.[20] The absorbing rate as well as the effects of mixture temperature and mixture concentration on absorbency was investigated. The relationship between the absorbency and the parameters of the mixing solvents were also investigated.

EXPERIMENTAL

Materials

Sodium hydroxide (analytical grade; Shanghai Chemical Reagent Factory, China), potassium persulfate (KPS) (analytical grade; Shanghai Chemical Reagent Factory), and triethylene glycol diacrylate (TEGDA) (Nakarai Chemical Ltd., Tokyo, Japan) were used as received. Acrylic acid (Shanghai Wulian Chemical Factory, China) was distilled under reduced pressure before use.

Methanol, ethanol, EG, glycerol, acetone, DMF, and DMSO were analytical grade, supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China), and used as received.

Preparation of Polyacrylate Superabsorbent

In a 500-mL beaker, cooled with 25°C recycled water bath, 31 g distilled water was mixed with 73.4 g acrylic acid. The stirred acrylic acid aqueous solution was neutralized by adding dropwise a sodium hydroxide aqueous solution (32.6 g sodium hydroxide and 72.2 g distilled water). KPS (0.291 g) and TEGDA (0.216 g) were dissolved in the monomer mixture at ambient temperature under full stirring. The aqueous monomer mixture was poured into a 30 $\times$ 30 cm polyethylene bag with a film thickness of 13.1 μm. The bag containing the monomer mixture was sealed with a heat-welting machine and then sandwiched vertically between a pair of stainless steel plates (rectangular, 35 $\times$ 9 $\times$ 0.15 cm). The distance between the two parallel plates was 1 cm, maintained by setting four stainless steel cubes with a side length of 1 cm in the four corners between the plates and clamping the plates with four clamps. The moored reaction device was vertically submerged in a 70°C water bath. The shape of the monomer mixture was about 30 $\times$ 6 $\times$ 1 cm. The monomer mixture was polymerized *in situ* for 1 h and a polymeric gel was formed. The product was cut into small pieces and then dried in a vacuum at 105°C for 8 h. The dried polymer was milled and then screened. Particles between 40- and 80-mesh were collected and labeled as SA1.

Swelling Measurement

Typically, SA1 (about 0.5 g) was immersed in 200 g distilled water in a 400-mL wide-mouth bottle with a closing plug and allowed to soak for some time at 25°C. The swollen gel was then separated from unabsorbed water by screening through a 120-mesh sieve and allowed to drain for 90 s. The sieve was then weighed to determine the weight of the swollen gel. The absorbency (Q) was calculated using the following equation:

$$Q = (W_2 - W_1)/W_1 \qquad (1)$$

where W_2 and W_1 are the weights of the swollen gel and the dry resin, respectively. Q was calculated as grams of water per gram of resin. Q (10 min) and Q (48 h) are referred to as the absorbency in 10 min and 48 h soaking, respectively.

RESULTS AND DISCUSSION

Absorbing Rate in Solvent–Water Mixtures

The absorbing rate of SA1 in the seven solvent–water mixtures at 20% concentration was shown
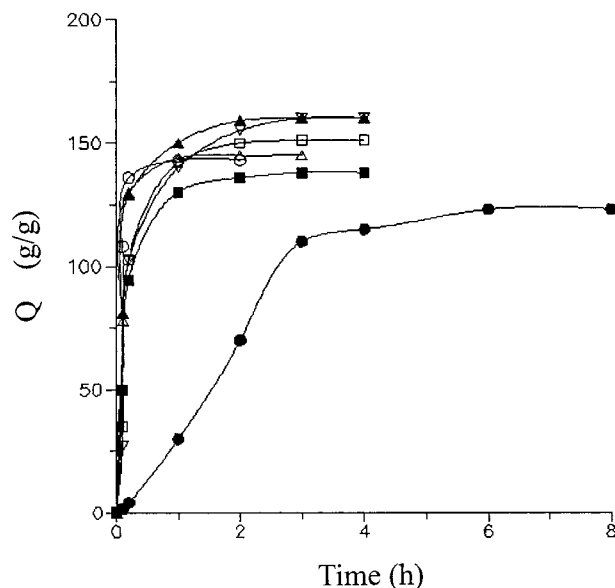
Figure 1 The absorbing rate of SA1 in 20 wt % solvent–water mixtures at 25°C: (■) methanol, (●) ethanol, (△) EG, (▽) glycerol, (○) acetone, (□) DMF, (▲) DMSO.

Figure 2 The effect of temperature of 20 wt % mixture on absorbency in 10 min: (■) methanol, (●) ethanol, (△) EG, (▽) glycerol, (○) acetone, (□) DMF, (▲) DMSO.

in Figure 1. The absorbency in the ethanol–water mixture increased continuously during the first 3 h and then increased rather slowly. The absorbency did not change at all when the soaking time was higher than 6 h, and the soaking time could be regarded as the time for SA1 to reach absorbing equilibrium. The absorbency in the acetone–water mixture and EG–water mixture could reach equilibrium in 1 and 2 h, respectively, whereas the absorbency in the other four mixtures could reach equilibrium in 3 h. The time reaching absorbing equilibrium for superabsorbents should also be relevant to their granularity.

The Effect of Mixture Temperature on Absorbency

The effect of mixture temperature in the range of 15 and 35°C on absorbency in 10 min was shown in Figure 2. The absorbency increased little for all seven mixtures. The diffusion rate is higher when the temperature rises. Therefore, the absorbency in 10 min increased. However, the increase of absorbency was rather limited from the experimental results.

A further experiment was conducted to find the temperature effect on absorbency of SA1 in distilled water in a wider temperature range. The result is listed in Table I. The change of absorbency was rather small when the water temperature ranged from 0.5 to 60°C, whereas the ab-
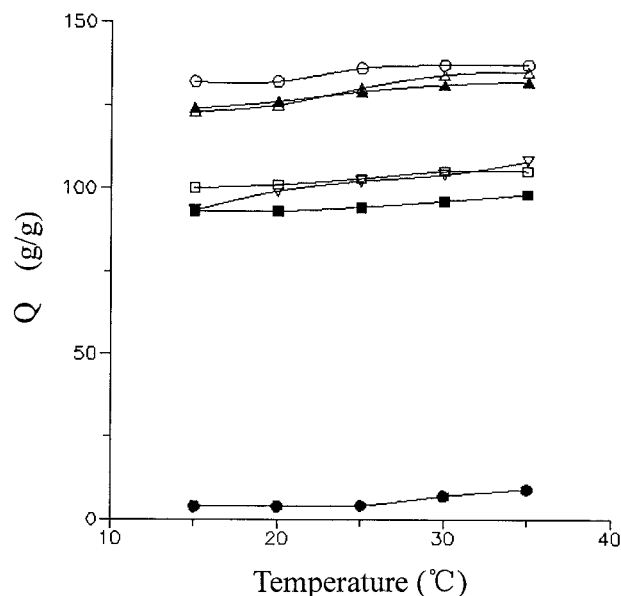
sorbency decreased from 172 to 100 when water temperature increased from 60 to 99°C.

Liu and Rempel[19] reported a similar result for the effect of mixture temperature on absorbency, although the extent of the effect in their study was higher than the extent in our study. The reason for the different extent of the effect might be that the absorbing capacity to distilled water of their poly(acrylate acrylamide) superabsorbent was about 760, much higher than 168 of SA1 in our study.

Absorbency of SA1 in the Seven Solvent–Water Mixtures

The absorbency of SA1 in the seven solvent–water mixtures was shown in Figures 3–9; curve a and b are referred to as the absorbency in 10 min [Q (10 min)] and 48 h [Q (48 h)], respectively. According to the absorbing characteristics in Figure 1, curve a and b in Figures 3–10 could be approx-

Table I The Effect of Temperature of Distilled Water on Absorbency in 10 min

Water temperature	(°C)	0.5	20	40	60	80	99
Absorbency	(g/g)	170	168	170	172	162	160

Figure 3   Absorbency of SA1 in methanol–water mixtures at 25°C: (a) 10 min, (b) 48 h.

Figure 4   Absorbency of SA1 in ethanol–water mixtures at 25°C: (a) 10 min, (b) 48 h.

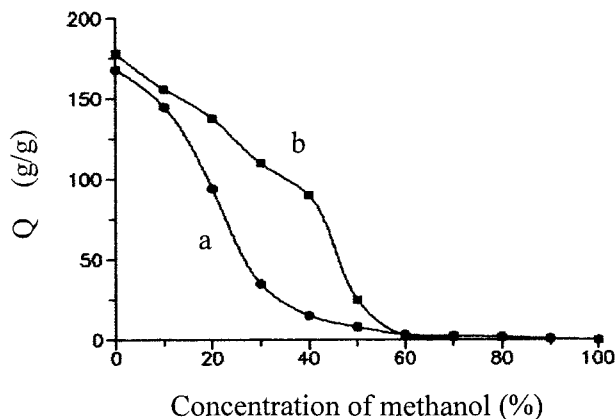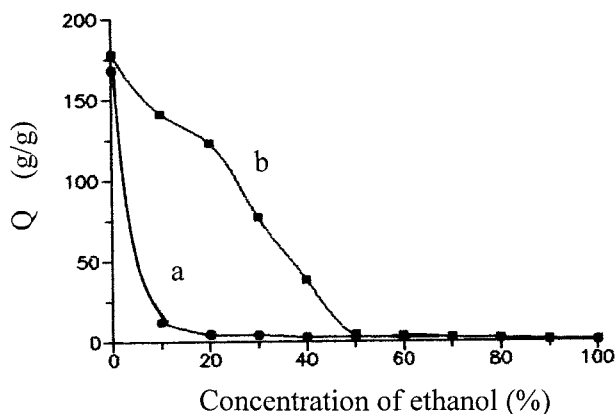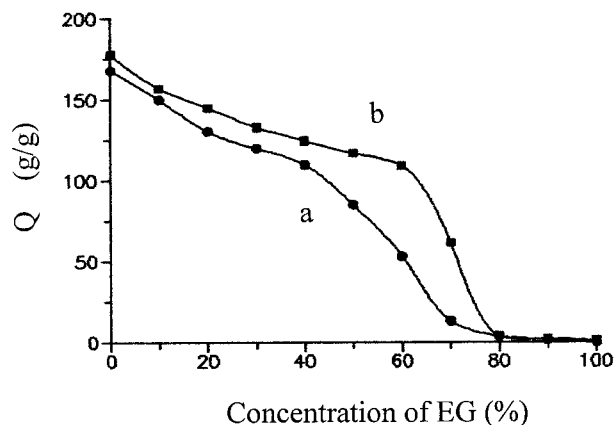**Figure 5**   Absorbency of SA1 in EG–water mixtures at 25°C: (a) 10 min, (b) 48 h.

imately regarded as the short-time absorbing capacity and the equilibrium absorbing capacity, respectively.

In Figure 3, Q (10 min) dropped from 168 to 3.2 when the methanol concentration was increased from 0 to 60%. If the concentration increased further, Q (10 min) decreased gradually to zero. Q (48 h) was greater than Q (10 min) when the methanol concentration was < 60%; however, Q (48 h) was almost the same as Q (10 min) when the methanol concentration was > 60%.

In Figure 4, Q (10 min) decreased quickly even when a small amount of ethanol was added to water. Q (10 min) dropped from 168 to 12 when the concentration of ethanol was increased from 0 to 10%. When the concentration was further increased, Q (10 min) gradually dropped to zero. Q (48 h) was much greater than Q (10 min) when the concentration was between 0 and 50%. Simi-

lar to Figure 3, Q (48 h) was almost equal to Q (10 min) when the ethanol concentration was > 60%. A similar tendency to curve b in Figures 3 and 4 was also reported by Murase and Fujita.[18]

In Figure 5, Q (10 min) decreased slowly in a wide concentration range, and this illustrated that SA1 had a higher absorbency to EG–water mixtures, compared with curve a in Figures 3 and 4. The reason might be that the soluble parameter of EG was much higher than that of methanol and ethanol, and also closer to that of water. The effect of the soluble parameter on absorbing capacity was discussed in detail in the following section. At the same concentration, Q (48 h) increased with different extents compared with Q (10 min) when the concentration was < 80%. Q (48 h) was equal to Q (10 min) when the concentration was > 80%.

In Figure 6, SA1 had a wide absorbable concentration range to glycerol–water mixtures. Q (10 min) decreased from 168 to 102 when the concentration of glycerol was increased from 0 to 20%. Q (10 min) decreased slowly when the concentration increased from 20 to 70%. Q (10 min) decreased faster when the concentration was > 70%. Q (10 min) was 2.1 for 100% glycerol. Compared with Q (10 min), Q (48 h) also had a certain increase when the concentration was < 90%. Q (48 h) was equal to Q (10 min) when the concentration was > 90%.

In Figure 7, curve a and b were very close, illustrating very high absorbing speed when acetone–water mixtures were absorbed by SA1; the result was also demonstrated in Figure 1. Q (10 min) dropped from 168 to 2.8 in Figure 7 when the concentration of acetone was increased from 0 to
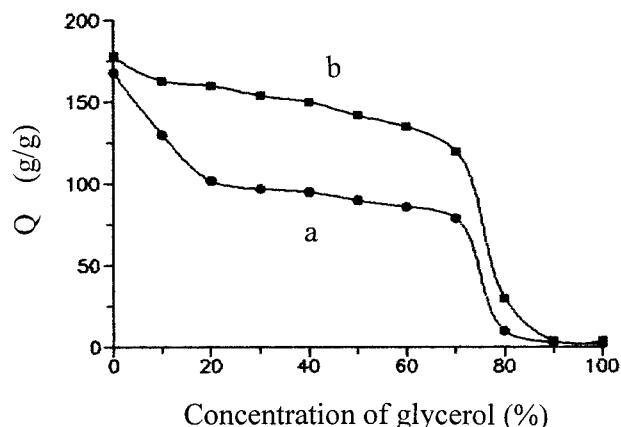
Figure 6 Absorbency of SA1 in glycerol–water mixtures at 25°C: (a) 10 min, (b) 48 h.

Figure 8 Absorbency of SA1 in DMF–water mixtures at 25°C: (a) 10 min, (b) 48 h.

40%. A very sharp drop occurred between 20 and 40%. The absorbency was very low when the concentration was between 40 and 100%.

In Figure 8, Q (10 min) decreased from 168 to 2.0 when the concentration of DMF was increased from 0 to 40%. The absorbency was very low for the concentration range from 40 to 100%. Compared with Q (10 min), Q (48 h) also had a certain increase when the concentration was < 60%. Q (48 h) was almost equal to Q (10 min) when the concentration was > 60%.

In Figure 9, Q (10 min) dropped sharply from 129 to 7.7 when DMSO concentration was between 20 and 40%. When the concentration was further increased, Q (10 min) decreased gradually to zero. Q (48 h) had a certain increase when the concentration was < 60%. Q (48 h) was almost equal to Q (10 min) when the concentration was > 60%.
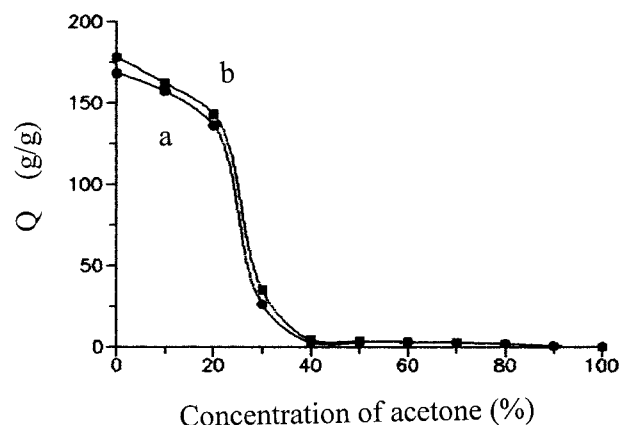
The Characteristics of the Swelling of SA1 in Hydrophilic Solvent–Water Mixtures

There are several common features between the swelling behavior of a crosslinked polymer in solvent and the dissolving of the linear polymer in the solvent. A solvent that can dissolve a linear polymer could also swell the polymer network. Therefore, the swelling of polymer networks would conform to the dissolving rules of linear polymers or the Hildebrand equation[21]:

$$\Delta H_M/(V\phi_1\phi_2) = (\delta_1 - \delta_2)^2 \qquad (2)$$

where ΔH_M is the enthalpy change on mixing of a polymer and a solvent, V is the whole volume of the solution, ϕ_1 and ϕ_2 are the volume fractions for the solvent and the polymer, and δ_1 and δ_2 are

Figure 7 Absorbency of SA1 in acetone–water mixtures at 25°C: (a) 10 min, (b) 48 h.

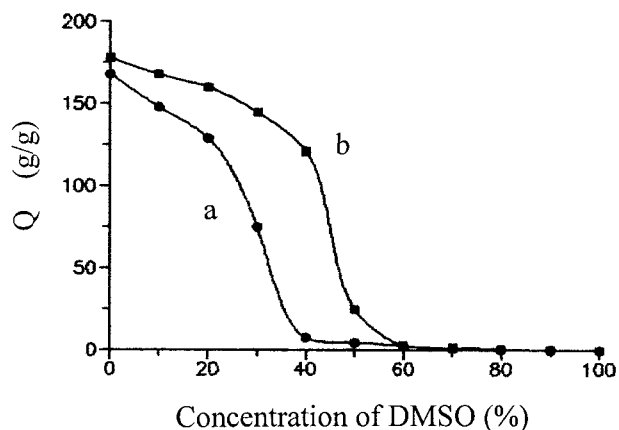**Figure 9** Absorbency of SA1 in DMSO–water mixtures at 25°C: (a) 10 min, (b) 48 h.

Table II Q (10 min) and Q (48 h) of SA1 in the Mixing Solvents at Concentration of 20, 40, and 60%, Respectively

	δ	P	δ_{20}	20% Q (10 min)	Q (48 h)	δ_{40}	40% Q (10 min)	Q (48 h)	δ_{60}	60% Q (10 min)	Q (48 h)
Acetone	10.0	0.695	20.0	136	143	17.2	2.8	4.5	14.6	2.2	3.2
DMF	12.1	0.772	20.9	103	156	18.6	2.0	40.1	16.4	1.9	4.8
Ethanol	12.7	0.268	20.7	4.5	123	18.4	2.6	38.2	16.3	2.3	3.4
DMSO	13.4	0.813	21.4	129	160	19.5	7.7	121	17.5	2.7	3.0
Methanol	14.5	0.388	21.1	94.2	138	19.2	15.2	90.1	17.5	2.9	3.1
EG	15.7	0.476	21.8	130	145	20.4	110	125	18.9	53.1	109
Glycerol	16.5	0.468	22.1	102	160	20.9	95.0	150	19.6	86.0	135

the solubility parameters for the solvent and the polymer.

The above equation predicts that a solvent can dissolve a polymer if the solubility parameters for the solvent and the polymer are close to each other. The polyacrylate superabsorbent has the highest absorbency when water is absorbed. The solubility parameter for water is 23.2 and this value can be regarded as the solubility parameter for SA1.

The following equation can be used to calculate the solubility parameter for a mixing solvent (δ_{mix})[20]:

$$\delta_{mix} = \phi'_1\delta_1 + \phi'_2\delta_2 \qquad (3)$$

where ϕ'_1 and ϕ'_2 are the volume fraction for the two solvents, and δ_1 and δ_2 are the solubility parameters for the two solvents.

Q (10 min) and Q (48 h) of SA1 in the mixtures of water and the seven hydrophilic solvents were

listed in Table II. δ_{20}, δ_{40}, and δ_{60} are referred to as the solubility parameters for the mixing solvent at a concentration of 20, 40, and 60%, respectively.

At a concentration of 20%, δ_{20} for acetone was 20 and δ_{20} for the other solvents were all > 20. Q (48 h) or equilibrium absorbency was very high. The relationship between Q (10 min) and δ_{20}, as well as the relationship between Q (48 h) and δ_{20}, was not clear. The phenomenon might be related to very high δ_{20} for the seven solvent–water mixtures at 20% concentration. The polarity fraction had a certain effect on Q (10 min) and Q (48 h). For example, Q (10 min) and Q (48 h) for methanol and ethanol were all smaller than that for other solvents and the polarity fraction of methanol as well as ethanol was much lower than that of other solvents. Particularly, the Q (10 min) for ethanol with the lowest polarity fraction was rather small, and the result illustrated that much low polarity fraction of solvent could decrease the absorbing capacity in short soaking time and
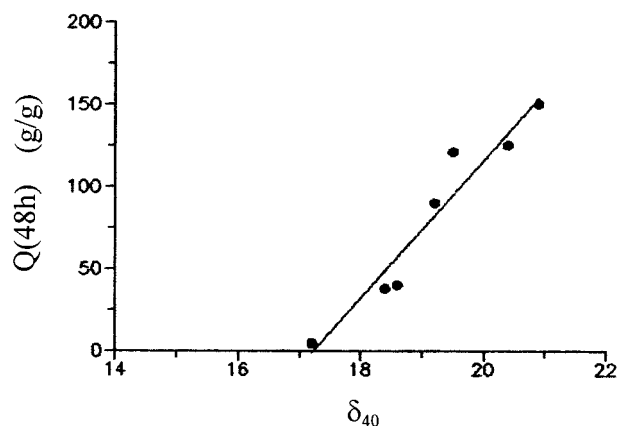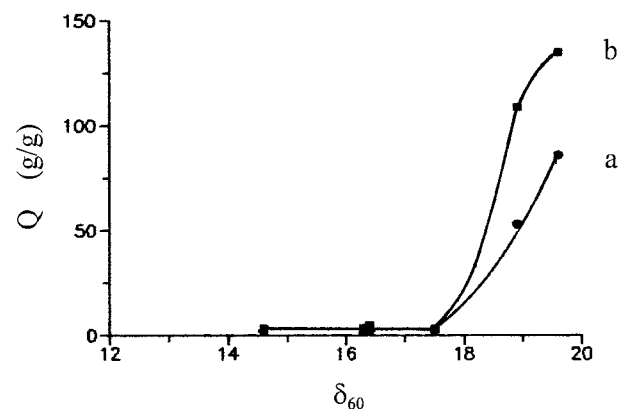

Figure 10   The effect of δ_{40} on absorbency within 48 h, 25°C.

Figure 11   The effect of δ_{60} on absorbency (Q), 25°C: (a) 10 min, (b) 48 h.

Table III   Comparison of C_{1C} and C'_{1C} for the Seven Solvent–Water Mixtures

	Acetone	DMF	Ethanol	DMSO	Methanol	EG	Glycerol
ϕ_{1C}[a]	0.432	0.514	0.543	0.582	0.655	0.760	0.851
C_{1C} (%)[a]	37.5	50.1	48.4	60.5	60.0	78.2	87.8
C'_{1C} (%)[b]	40	50–60	50	60	60	80	80–90

[a] ϕ_{1C} and C_{1C} were calculated from eq. (3) with $\delta_C = 17.5$.
[b] C'_{1C} was the concentration at the transition point via extrapolation from high concentration to low concentration in Figures 3–9.

lower the absorbing speed even though the solubility parameter for the mixture was very high.

At a concentration of 40%, δ_{40} was all lower than δ_{20}; only δ_{40} for EG and glycerol were higher than 20. Q (10 min) was still high when δ_{40} was > 20. However, Q (10 min) was rather small when δ_{40} was < 18.6. The result reflected the fact that the absorbing capacity in short soaking time was decided by the solubility parameter. The relation between Q (48 h) and δ_{40} was shown in Figure 10. Q (48 h) increased with δ_{40}. The equilibrium absorbency was decided by solubility parameter when solubility was between 17.2 and 20.9.

At a concentration of 60%, the solubility parameters were all < 20. The effect of δ_{60} on absorbency was shown in Figure 11; curve a and b are referred to as the absorbency in 10 min and 48 h, respectively. Curve a and b matched together when δ_{60} was < 17.5, with a rather low absorbency of not more than 5. Only EG and glycerol had solubility parameters > 17.5; the values were 18.9 and 19.6, respectively, still having good swelling ability to SA1. The results further illustrated that the absorbency of SA1 to the mixtures was decided by solubility parameters when the solubility parameter was between 14.6 and 19.6.

From Figure 11, the absorbency changed greatly when the solubility parameter was near 17.5. The 17.5 value could be regarded as a critical solubility parameter (δ_C). SA1 had limited absorbency when the solubility parameter was lower than δ_C. With eq. (3), the critical volume fraction (ϕ_{1C}) and critical concentration (C_{1C}) for a solvent could be calculated when $\delta_C = 17.5$ was put in eq. (3). From Figures 3–9, curve b at high concentration was approximately a straight line; a transition point could be obtained via extrapolation from high to low concentration. The concentration at the transition point was experimental critical concentration (C'_{1C}). The results were listed in Table III. C'_{1C} was very close to C_{1C}. So

it was reasonable that 17.5 was regarded as the critical solubility parameter or the criterion of the absorbing capacity of SA1 in organic solvent–water mixture.

CONCLUSIONS

The swelling behaviors of polyacrylate superabsorbent in the mixtures of water and hydrophilic solvents, including methanol, ethanol, EG, glycerol, acetone, DMF, and DMSO, were investigated. Mixture temperature had limited influence on water absorbency. The addition of hydrophilic solvent in water reduced the water absorbency of the superabsorbent. Such influence was due to changes of solubility parameter of solvent–water mixtures. Results indicated that equilibrium absorbency was very high when the solubility parameter of mixtures was > 20, whereas the absorbing capacity of the superabsorbent was very low when the solubility parameter was < 17.5. It was found that 17.5 was the criterion of absorbing capacity of the polyacrylate superabsorbent in organic solvent–water mixtures. The polarity fraction of solvents might affect the absorbing rate rather than the equilibrium absorbency.

REFERENCES

1. Tanaka, H.; Kambayashi, T.; Sugiyama, Y.; Nagai, T.; Nagata, K.; Kubota, K.; Hirano, K. Eur. Pat. 501,482, 1992.
2. Miura, Y.; Hirano, K.; Nate, T.; Kambayashi, T.; Ohtsuka, M.; Nagai, T. Eur. Pat. 440,256, 1991.
3. Shimomura, T.; Namba, T. in Superabsorbent Polymers, Buchholz, F. L.; Peppas, N. A., Eds.; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1994.
4. Honda, N.; Wakumoto, H.; Nakano, T.; Ueki, H.; Hiratsuka, J. Eur. Pat. 122,797, 1984.
5. Clarke, J. B. Eur. Pat. 101,253, 1984.

6. Tsuji, S.; Musika, H.; Itoh, M.; Saga, J.; Fujiwara, T.; Hatsuda, T. Eur. Pat. 356,161, 1990.
7. Walker, C. O. U.S. Pat. 4,664,816, 1987.
8. Hefner, R. E.; Haynes, D. I. U.S. Pat. 4,611,015, 1986.
9. Hosoya, Y.; Watanabe, N.; Takagi, I.; Miyoshi, A. Eur. Pat. 342,996, 1989.
10. Katzer, M. F. U.S. Pat. 3,354,084, 1967.
11. Tsubakimoto, T.; Shimomura, T.; Kobayashi, H. Jpn. Pat. 62,149,335, 1987.
12. Tanaka, K. Kogyo Zairyo 1994, 42(4), 18.
13. Ende, M. T.; Hariharan, D.; Peppas, N. A. React Polym 1995, 25, 127.
14. Conte, U.; LaManna, A.; Giunchedi, P. Eur. Pat. 468,392, 1992.
15. Lee, W. F.; Wu, R. J. J Appl Polym Sci 1997, 64, 1701.
16. Lee, W. F.; Wu, R. J. J Appl Polym Sci 1997, 64, 2371.
17. Smith, P. B.; Cutie, S. S.; Henton, D. E.; Powell, C.; Kosman, J.; Howell, B. A. J Polym Sci, Part A: Polym Chem 1997, 35, 799.
18. Murase, I.; Fujita, B. Kogyo Zairyo 1981, 29(8), 34.
19. Liu, Z. S.; Rempel, G. L. J Appl Polym Sci 1997, 64, 1345.
20. He, M.; Chen, W.; Dong, X. Macromolecular Physics, revised ed.; Fudan University Press: Shanghai, 1990.
21. Hilderbrand, J.; Scott, R. L. Solubility of Nonelectrolytes; Reinhold Publishing: New York, 1949.