Swelling Equilibria of Polymeric Hydrogels Containing Poly(acrylamide-sodiumallylsulfonate-acrylic acid)

Nam-Hyung Kim, Tae Hyung Lee and Joong So Choi†

Department of Chemical Engineering, Institute of New Technology, Kwangwoon University,
447-1, Wolgyedong, Nowonku, Seoul 139-701, Korea
(*Received 30 December 1999 • accepted 24 August 2000*)

Abstract−The superabsorbent poly(AM-SAS-AA)s were synthesized to improve the water absorption capacities in comparison with the poly(AM-SAS) by an aqueous solution polymerization method from acrylamide (AM), sodium allylsulfonate (SAS), and acrylic acid (AA). The reaction conditions were controlled by varying the AA concentrations and fixing other agent concentrations to obtain the optimal superabsorbent poly(AM-SAS-AA). The poly(AM-SAS-AA) showed maximal absorption capacity at 0.3 mol/L among AA concentrations from 0.053 mol/L to 0.4 mol/L. The water absorption capacities of poly(AM-SAS-AA)s prepared at the optimal reaction condition were measured within the temperature ranges from 298.15 K to 318.15 K. Those experimental data were used to describe the effect factors on absorption capacities and swelling equilibria data among those data were correlated with the swelling models to estimate the interchange energy parameters. Each swelling models combined with group contribution models (UNIFAC, ASOG) was introduced to calculate the swelling equilibria of water(1)/poly(AM-SAS-AA)(2) systems. The swelling behaviors could be described by the estimated parameters, and the calculated values agreed well with the experimental data.

Key words: Superabsorbent, Aqueous Solution Polymerization, Absorption Capacities, Swelling Model, Swelling Equilibria

INTRODUCTION

Natural fibers or urethane sponges absorb only a few times the water against their weight and the absorbed water is easily released under external pressure [Brannaon-Peppas and Peppas, 1988, 1991; Buchholz and Peppas, 1993]. The new materials which were called as the superabsorbent polymers (SAP) have been developed to apply to various industries because they absorb much water in comparison with the previous water absorption materials. They absorb a few hundreds to thousands of times water and have the characteristic of keep the water in the network structure under external pressure [Liu and Remple, 1996]. The SAPs have the broad uses for industrial applications [Yao and Zhou, 1994] such as sanitary materials, diapers, agriculture fields, medicines, and other advanced technologies.

There were many researches about the preparation of superabsorbent polymers or the polymerization methods because of their various applications to industries. Parks [1981] prepared the absorbent polyacrylate by copolymerizing AA with a divinyl crosslinker such as tetraethylene glycol diacrylate in about 10% aqueous solution, with sodium persulfate as the initiator at 60 °C. Yoshida et al. [1982] synthesized the same absorbent polyacrylates obtained by polymerizing sodium acrylate in 16% aqueous solution, in the presence of poly(ethylene glycol diglycidyl ether) as the crosslinker. Yamasaki and Harada [1984] and Stanley et al. [1987] studied the suspension polymerization process to synthesize the absorbent polyacrylate which employed the combination of hydrophobic silica and copolymer of AA and lauryl methacrylate as the suspension agent. Chang et al. [1999] have synthesized the poly(AM-SAS) from AM and SAS and suggested its opimal synthesis conditions.

In this work, we prepare the superabsorbent poly(AM-SAS-AA)s to improve its water absorption capacities in comparison with the poly(AM-SAS) of Chang et al. [1999] by an aqueous solution polymerization method from AM, SAS and AA, and supply the optimal synthesis conditions, and consider the swelling equilibria of them. The water absorption capacities of the prepared superabsorbent poly(AM-SAS-AA)s would be measured by immersing in the water and compared with the previous work [Chang et al., 1999] for the water(1)/poly(AM-SAS-AA)(2) systems. They would be used to estimate the interchange energy parameters by being correlated with the swelling models combined by the group contribution model (ASOG, UNIFAC) to express the mixing in the bulk phase and three kinds of equations to do equally the elastic deformation in polymeric network, respectively. And the estimated interchange energy parameters would be used to describe the swelling behavior of polymeric hydrogels named as poly(AM-SAS-AA) in water.

EXPERIMENTAL

1. Reagents

Acrylamide and sodiumallylsulfonate were purchased from Aldrich Chemical and used without further purification. Acrylic acid was delivered from Junsei Chemical and distilled to remove impurities under vacuum. It was stored at 10 °C until requirement after distillation. Potassium persulfate (PP), N,N,N',N'-tetramethylenediamine (TMEDA) and N,N'-methylenebisacrylamide (MBISAM) were also respectively purchased from Sigma and Aldrich Chemical. They were used as received and water was also used after re-

†To whom correspondence should be addressed.
E-mail: jschoi@daisy.kwangwoon.ac.kr

distillation.

2. Preparation of Poly(AM-SAS-AA)

The synthesis apparatus consists of a water bath with (±0.01 °C accuracy), 1 L rounded flask, mechanical stirrer with teflon material, nitrogen bomb, condenser, and thermometer. The schematic synthesis apparatus was represented in previous work [Chang et al., 1999]. The synthesis was carried out in nitrogen atmosphere for pure and high quality polymer product.

The respective AM and SAS concentrations were fixed on 0.97 mol/L and 0.04 mol/L and the AA concentration varied from 0.053 mol/L to 0.4 mol/L during the synthesis of poly(AM-SAS-AA). PP, TMEDA and MBISAA were also fixed at the each concentration that was 0.00267 mol/L, 0.003 mol/L and 0.0064 mol/L, respectively. The aqueous solution containing all reagents was de-aerated to prevent trivial reactions with nitrogen by stirring continuously for 25 min during the synthesis procedure. The 0.1 N NaOH was added and an aqueous solution adjusted to pH 4. The superabsorbent poly(AM-SAS-AA) was obtained after the solution was continuously stirred for 2 h at 313.15 K. The product was dehydrated with ethanol and dried for 12 h at 323.15 K in a vacuum oven until constant weight was kept. The product was milled and screened through the 60 mesh screen.

3. Measurement of Absorption Capacities

The prepared poly(AM-SAS-AA) powders were accurately weighed to 0.2 g (m_1) and immersed in distilled water at each experimental temperature. The swollen poly(AM-SAS-AA)s were respectively separated from the water by screening through the tared 60 mesh sieve and allowed to drain for 10 min. And weighed (m_2) after removing the remaining surface water of polymer again screened through the 60 mesh sieve. The samples were repeatedly reweighed at 10 min intervals until they were reached at equilibrium approached.

The swelling capacities were determined from Eq. (1) as follows:

$$\text{Absorption Capacity (Q)} = \frac{m_2 - m_1}{m_2} \tag{1}$$

The volume fractions of each component in the polymeric hydrogels absorbing the water were determined from the following Eq. (2).

$$\phi = \frac{\dfrac{m_i}{\rho_i}}{\sum_j \dfrac{m_i}{\rho_i}} = \frac{v_i}{\sum_j v_i} \tag{2}$$

where the measured densities (ρ_i) are listed in Table 1 and the volume fractions on swelling equilibria among all of absorption capacities listed in Table 2.

RESULTS AND DISCUSSION

Table 1. Densities of water and polymers measured

Materials	298.15	303.15	308.15	313.15	318.15
Water	0.997	0.996	0.994	0.992	0.99
Polymer(AM-SAS-AA)	0.645	0.645	0.645	0.645	0.645

Table 2. Experimental volume fractions of each component for water(1)/poly(AM-SAS-AA) (2) systems on swelling equilibria

T (K)	ϕ_1	ϕ_2
298.15	0.9996	0.0004
303.15	0.9997	0.0003
308.15	0.9997	0.0003
313.15	0.9998	0.0002
318.15	0.9998	0.0002

1. Effect Factors on Absorption Capacities

There are many factors that have an effect on the absorption capacities of superabsorbent polymer in water. In a series of investigations of the preparation and properties of superabsorbent polymers, a number of aspects have been explored, such as the ulimate capacity for absorbing water, rate of absorption and the dependence of absorption on monomer composition, degree of crosslinking, type of crosslinker and type of polymerisation process, as well as on temperature and initiator concentration. Generally the water absorption characteristic of nearly all polymers is a result of the strong affinity toward water of the polar sites on the polymer chains and the existence of crosslinks, which are able to maintain the network structure. In other words performance for water absorption of polymers is largely dependent on the hydrolytic stability of the polymers, the mechanical properties of the hydrated structure and the absorbed water properties. These bonds maintaining the hydrated state occur in general between hydrogen and the electronegative elements nitrogen, oxygen, and fluorine, termed proton acceptors, where the electron density of the hydrogen atom will decrease by interaction with unbonded electron pairs of these proton acceptors. These characteristic polar groups contain nitrogen and/or oxygen as potential proton acceptors to form hydrogen complexes. Because in microscopic view hydrogel swelling is induced mainly by the electrostatic repulsion of ionic charges in the network, the content of which is determined by the ratio of feed monomers, the swelling increase is due to an increase of the anionic monomer having strong reactive group between/among components constituting copolymer, but an excess of ionic units leads to an increase in the soluble material. Absorption capacities are generally increased by having large hydrophilic groups in polymeric network but decreased with raising the ion concentrations or the crosslink densities [Buchholz and Peppas, 1993; Yoshida et al., 1982].

Yao and Zhou [1994] and Zhou et al. [1996] synthesized the poly(acrylamide-sodium acrylate-sodium allylsulfonate) and it showed the maximal 437 times water absorption capacity. In this work, anionic acrylic acid was empirically considered as more important factor for water absorption because it is cheap and easy to polymerize to products of high molecular weight and have more small reactive group than sodium acrylate (steric effect), and its optimal concentration was needed to be determined because the concentration of three kinds of monomers showed mutual dependency, we could increase the absorption capacities by attaching the large hydrophilic groups (acrylic acid) instead of their anionic monomer (sodium acrylate) of poly(acrylamide-sodium acrylate-sodium allylsulfonate). Those results were plotted Fig. 1. Fig. 1 showed the water absorption capacities of six kinds of poly(AM-SAS-AA)s ac-
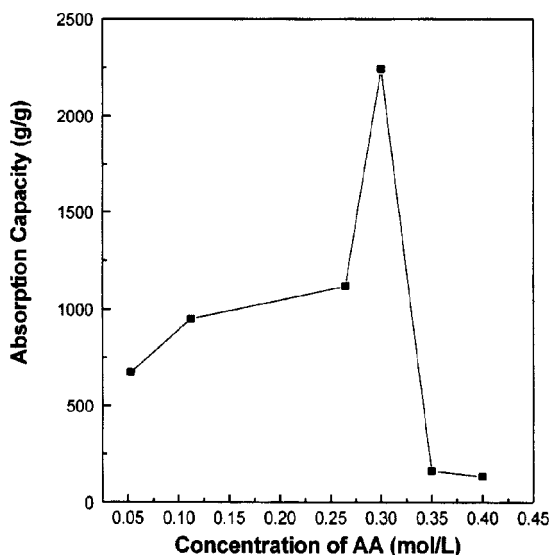
Fig. 1. Determination of the optimal absorption capacities of poly(AM-SAS-AA) at 298.15 K.

cording to the variations of AA concentrations from 0.053 mol/L to 0.4 mol/L. As shown in Fig. 1, all of water absorption capacities of poly(AM-SAS-AA) were larger than those of poly(acrylamide-sodium acrylate-sodium allylsulfonate). Its maximal value was 2284 times when AA concentration was 0.3 mol/L. Those results proved that the absorption capacities could be increased by substituting the hydrophilic monomer for the anionic monomer. Those improvable effect was also resulted in the addition of hydrophilic monomer to the previous SAP ploy(AM-SAS) [Chang et al., 1999]. Their results are plotted on Fig. 2. As shown in Fig. 2, poly(AM-SAS-AA) improved in the absorption capacity more than about three times in comparison with those of poly(AM-SAS).

On the other hand, the absorption capacities must be influenced by the hydrophilic groups but there were other effect factors such
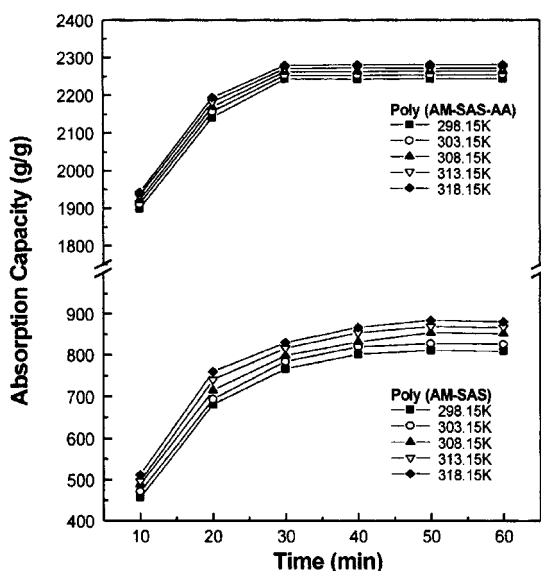
as initiator concentration, crosslinker concentrations, pH, and temperature. Among those conditions, the temperature especially had the greatest influence on the absorption capacities [Yamasaki and Harada, 1984] excepting the monomer concentrations. Temperature dependence of water absorption is explained that when crankshaft motion in polymer chain start, thermal expansion should be increased because more space is formed in polymer chain. The space can be called free or interstitial volume which serves to accommodate additional water by a typical capillary action. The response to temperature change varied with the porosity of the polymer gel, which they assumed influenced heat transfer and network diffusion. Clearly, for polymeric materials of identical composition but varying porosity, porosity may be able to explain the difference in water absorption. Those swelling behavior could be described by the data of swelling equilibria plotted on Fig. 2 for the polymeric hydrogels containing the superabsorbent poly(AM-SAS-AA) prepared in above optimal synthesis conditions. As shown in Fig. 2, those absorption capacities of the polymers were increased according to temperature increments from 298.15 K to 318.15 K because of the easy movement of the copolymer chains and increase of free volume in them.

2. Models of Swelling Equilibria

Swelling model which expresses swelling equilibria consists of the sum of the chemical potential changes due to mixing in the bulk phase and due to elastic deformation induced by an expansion of polymeric network structure [Flory, 1953]. When the superabsorbent poly(AM-SAS-AA) was swelled in the water at constant temperature and pressure, the relation in the chemical potential changes could be thermodynamically represented as follows: [Flory and Rehner, 1943a, b]

$$\Delta\mu_i = \Delta\mu_{i,\,mix} + \Delta\mu_{i,\,el} \tag{3}$$

Eq. (3) could be represented as Eq. (4) when the poly(AM-SAS-AA) having polymeric network structure reached swelling equilibria in the water.

$$\Delta\mu_{i,\,mix} + \Delta\mu_{i,\,el} = 0 \tag{4}$$

In this work, the group contribution models (ASOG, UNIFAC) were used to represent the chemical potential changes ($\Delta\mu_{i,\,mix}$) due to mixing in the bulk phase. They have been typically applied to predict the liquid-phase activity coefficients of low molecular or polymer solutions [Oishi and Prausnitz, 1978; Choi et al., 1995]. They must be combined with the equation of Panayiotou and Vera [1980] to represent the chemical potential change. Panayiotou and Vera [1980] proposed Eq. (5) to express the activity coefficient of arbitrary components in the bulk phase.

$$\ln\gamma_i = (\ln\gamma_i)^0 + \frac{zq_i}{2}\ln\Gamma_{ii} \tag{5}$$

In Eq. (5), $(\ln\gamma_i)^0$ s could be respectively represented by Eq. (6) for ASOG [Kojma and Tochigi, 1979] and Eqs. (7) to (10) for UNIFAC [Fredenslund et al., 1975] to obtain the change of chemical potential due to mixing in the bulk phase.

$$(\ln\gamma_i)^0 = \ln\frac{v_i^{FH}}{\sum_j v_j^{FH}x_j} + 1 - \frac{v_i^{FH}}{\sum_j v_j^{FH}x_j} \tag{6}$$

Fig. 2. Comparison of absorption capacities between poly(AM-SAS-AA) and poly(AM-SAS).

$$(\ln\gamma_i)^0 = \ln\frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{1}{2}zq_i\left(\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right) \qquad (7)$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j q_j} \qquad (8)$$

$$\theta_i = \frac{x_i r_i}{\sum_j x_j q_j} \qquad (9)$$

$$r_i = \sum_k \nu_{k,i} R_k, \quad q_i = \sum_k \nu_{k,i} Q_k \qquad (10)$$

$$x_i = \phi_i \frac{\rho_i}{M_i} \frac{\sum_j \frac{m_j}{\rho_j}}{\sum_j \frac{m_j}{M_j}} \qquad (11)$$

Therefore, Eq. (5) could be converted to Eq. (12) by using the thermodynamic relations, $a_i = x_i\gamma_i$ and $\Delta\mu_i = RT \ln a_i$.

$$\Delta\mu_{i,mix} = RT\left[(\ln\gamma_i)^0 + \frac{zq_i}{2}\ln\Gamma_{ii} + \ln x_i\right] \qquad (12)$$

The group volume parameters (R_k) and the group surface area parameters (Q_k) of in Eq. (10) were quoted from the work of Gmehling et al. [1982].

On the other hand, we quoted three kinds of equations to obtain the change of chemical potential ($\Delta\mu_{i,el}$) due to the elastic deformation in polymeric hydrogels. Flory [1953] proposed Eq. (13) to describe the elastic deformation of polymeric network structures.

$$\Delta\mu_{i,el} = RT\left[\frac{V_i}{v_2 M_c}\left(1 - \frac{2M_c}{M}\right)\left(\phi_2^{\frac{1}{3}} - \frac{\phi_2}{2}\right)\right] \qquad (13)$$

Eq. (13) was based on a Gaussian distribution of polymer chain length for water(1)/polymer(2) systems. Also, James-Guth [1943] proposed "phantom network" theory that is based on Gaussian distribution and the form was as follows:

$$\Delta\mu_{i,el} = RT\left[\frac{V_i}{2v_2 M_c}\left(1 - \frac{2M_c}{M}\right)\phi_2^{\frac{1}{3}}\right] \qquad (14)$$

Both Flory's expression [Eq. (13)] and the phantom network expression [Eq. (14)] were based on Gaussian probability distribution of polymer chain length, but Wall and White [1974] proposed elastic deformation term based on non-Gaussian probability distribution. Its form was given by:

$$\Delta\mu_{i,el} = RT\left[\frac{V_i}{v_2 M_c}\left(1 - \frac{2M_c}{M}\right)\left(\frac{5}{3}\phi_2^{\frac{1}{3}} - \frac{7}{6}\phi_2\right)\right] \qquad (15)$$

where the term ($1 - 2M_c/M$) that accounts for the deviation of real network from a perfect network was assumed as no dangling chain in poly(AM-SAS-AA). It led to $2M_c/M \ll 1$.

3. Calculation of Swelling Equilibria

When the water(1)/poly(AM-SAS-AA)(2) system reached swelling equilibrium, the chemical potential change of water in the polymeric hydrogels was given by Eq. (4). Eq. (4) was combined with the group contribution models (ASOG, UNIFAC) to express the change of chemical potential due to mixing and three kinds of equa-

tions to do identically the term due to elastic deformation on the swelling equilibria.

Therefore, Eq. (4) could be classified as six kinds of swelling models to calculate swelling equilibria for water(1)/poly(AM-SAS-AA)(2) systems after substituting Eq. (12) and one equation among Eqs. (13) to (15) for Eq. (4). For convenience sake, the swelling models were named as ASOG-Flory (AF), ASOG-James-Guth (AJG), ASOG-Wall-White (AWW), UNIFAC-Flory (UF), UNI-FAC-James-Guth (UJG), UNIFAC-Wall-White (UWW), respectively. To obtain the nonrandom factor Γ_{ii} in Eq. (4), an additional equation is needed to relate the nonrandom factors to the interchange energy (w_{ij}), which is defined as $w_{ij} = \varepsilon_{ij} - (1/2)(\varepsilon_{ii} + \varepsilon_{ij})$, where ε_{ij} is the interaction energy for the interaction between i and j molecule [Guggenheim, 1944]. We used Guggenheim's result [1944, 1952] which related the number of i–i, i–j, and j–j contacts to the interchange energy to evaluate the nonrandom factor. The equation between interchange energy parameters was represented as the following Eq. (16) [Prange et al., 1989; Gusler and Cohen, 1994]:

$$\frac{\Gamma_{ij}^2}{\Gamma_{ii}\Gamma_{jj}} = \exp(-2w_{ij}/kT) \qquad (16)$$

To ensure that the total number of contacts with molecules of type i is consistent with the total number of contact sites on molecules of type i, the following Eq. (17) is needed for each component in the mixture.

$$1 - \sum_{j\neq i}\theta_j\Gamma_{ij} - \theta_i\Gamma_{ii} = 0 \qquad (17)$$

The molecular weight between crosslinks, M_c, was determined by using Eq. (18) [Bell and Peppas, 1996].

$$M_c = \frac{M_r}{nX_{nom}} \qquad (18)$$

Here, M_r is the molecular weight of the repeating unit for the cross-linked polymer and is determined from the initial concentration ratio of AM, SAS, and AA. X_{nom} was used by the recommended value of Bell and Peppas [1996]. It is a typical value and $X_{nom} = 0.001$. Therefore, M_c was evaluated from Eq. (18) and its value $M_c = 71784.5$ for poly(AM-SAS-AA) of this work. It was fixed to estimate the interchange energy parameters of six kinds of swelling models during the calculation procedure.

The experimental volume fractions of swelling equilibria for the water(1)/poly(AM-SAS-AA)(2) systems in Table 2 were, respectively, correlated with Eq. (4) having six kinds of swelling models based on group contribution models to estimate the binary interchange energy parameters between water and poly(AM-SAS-AA). The computational procedures were described in detail in the work of Kim et al. [1998]. And the same fittings were carried out for the previous experimental data for water(1)/poly(AM-SAS) systems. The estimated parameters were showed in Fig. 3 to 4 to describe more visually the swelling equilibria of polymeric hydrogels containing the poly(AM-SAS-AA) or poly(AM-SAS) and average deviations are tabulated in Table 3, respectively. As shown in Fig. 3 to 4, interchange energy parameters (w_{12}/k) between water and poly (AM-SAS-AA) were increased according to the increments of temperature. The interchange energy parameters of poly(AM-SAS-AA)

Table 3. The average percent deviations between the experimental and the calculated volume fractions of polymer for water(1)/poly(AM-SAS-AA) (2) systems

T (K) \ Model	AJG[1]	AWW[2]	AWW[3]	UF[4]	UJG[5]	UWW[6]
298.15	0.0007	0.0007	0.0007	0.0013	0.0013	0.0013
303.15	0.0006	0.0006	0.0006	0.0015	0.0015	0.0015
308.15	0.0009	0.0009	0.0009	0.0011	0.0011	0.0011
313.15	0.0010	0.0010	0.0010	0.0010	0.0010	0.0010
318.15	0.0011	0.0011	0.0011	0.0014	0.0014	0.0014
Average	0.0009	0.0009	0.0009	0.0013	0.0013	0.0013

$$\text{Average Deviation (\%)} = \frac{1}{N}\sum_i \left(\frac{|\phi_{2,cal,i} - \phi_{2,exp,i}|}{\phi_{2,exp,i}}\right)$$
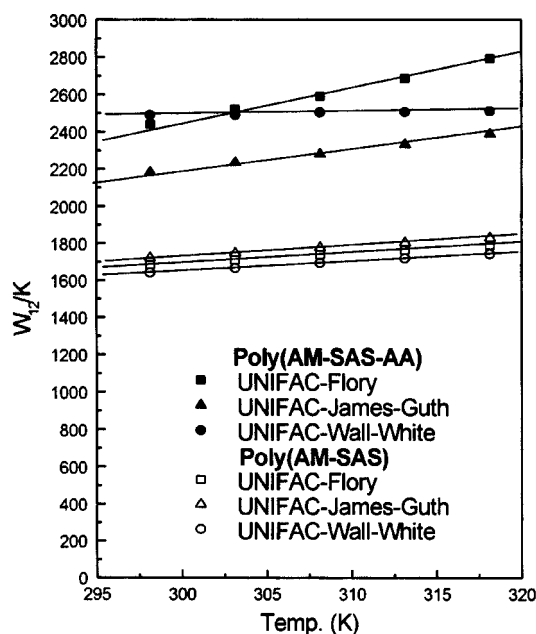
Fig. 3. Interchange energy parameters estimated by UNIFAC-based swelling models for water(1)/poly(AM-SAS-AA) [or poly(AM-SAS)](2) systems.

were greater than those of poly(AM-SAS) as shown in Fig. 3 in the case of UNIFAC-based swelling models. It meant that the poly(AM-SAS-AA) became more swellable than poly(AM-SAS) and more gelable by absorbing much water into the polymer. The additional descriptions about those swelling behaviors of poly (AM-SAS-AA) in the water were also supported by Fig. 4 in the case of ASOG-based swelling models. As shown in Fig. 4, the same trends were appeared in ASOG-based swelling models as well as UNIFAC-based swelling models. And the calculated values were satisfactory agreed with the experimental data as listed in Table 3.

In the computational procedures, the group interaction parameters of UNIFAC and ASOG were referred from the results of Gmehling et al. [1982] and Tochigi et al. [1990], respectively. The Marquardt method was used as the mathematical algorithm to calculate the swelling equilibria during the parameter estimation procedure. The volume fractions were calculated by minimizing the ob-
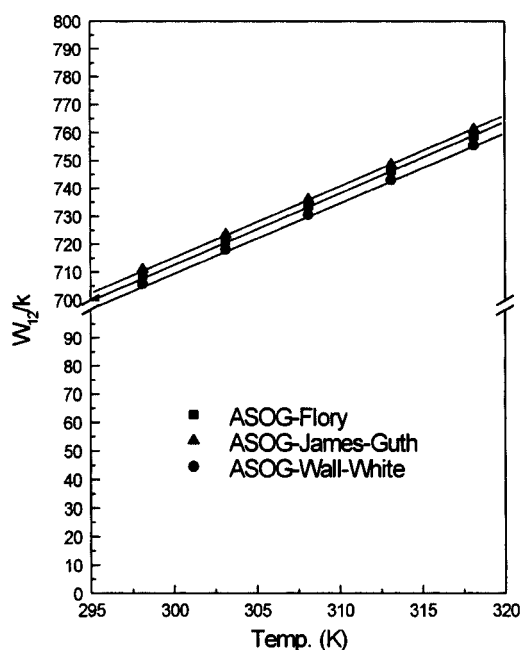
Fig. 4. Interchange energy parameters estimated by ASOG-based swelling models for water(1)/poly(AM-SAS-AA)(2) systems.

jective function $(\phi_i^{cal} - \phi_i^{exp})^2$ and the term $(1 - 2M_c/M)$ in three kinds of elastic deformation terms was taken to be unity, which was equivalent to assuming $2M_c/M \ll 1$.

CONCLUSIONS

The superabsorbent poly(AM-SAS-AA)s were prepared to improve absorption capacities in comparison with the poly(AM-SAS) from acrylamide, sodiumallylsulfonate, and acrylic acid. AA concentrations were varied from 0.053 mol/L to 0.4 mol/L during synthesis of the poly(AM-SAS-AA). When AA concentration was 0.3 mol/L, it showed the maximal absorption capacity among the AA concentration ranges. It was resulted in the maximal 2284 times in comparison with 811 times of poly(AM-SAS) for the absorption capacity by attaching the hydrophilic monomer to poly(AM-SAS) at the optimal synthesis conditions. Those results showed that the absorption capacities of poly(AM-SAS-AA) against the water were influenced by the concentrations of monomer having the hydrophilic group. And other major effect on the absorption capacities was temperature. They were also increased according to the increments of temperature from 298.15 K to 318.15 K.

On the other hand, the experimental swelling equilibria data were correlated with six kinds of swelling models to calculate the swelling equilibria for the water(1)/poly(AM-SAS-AA)(2) systems. The estimated interchange energy parameters showed increasing according to increments of temperature. It could describe that the poly(AM-SAS-AA) became more swellable than poly(AM-SAS), and more gelable by absorbing much water into the polymer. And the calculated values agreed with the experimental values within the average 0.0009%, 0.0013% deviations for water(1)/poly(AM-SAS-AA)(2) systems.

Therefore, we could explain the swelling behaviors of polymeric

gels with the estimated interchange energy parameters for water(1)/poly(AM-SAS-AA)(2) systems and could successfully apply the group contribution model to express the swelling equilibria in polymeric hydrogels containing poly(AM-SAS-AA).

ACKNOWLEDGMENT

NOMENCLATURE

a_i : the activity of component I
k : Boltzmann constant [KJ/mole K]
M : molecular weight of the crosslinked polymer
M_c : average molecular weight of the chain between crosslinked polymer [kg/mol]
M_r : molecular weight of the repeating unit for the crosslinked polymer [kg/mol]
n : number of functional sites for crosslinking agent [-]
q_i : volume parameter of component i
Q_k : group volume parameter of group k
r_i : surface area parameter of component i
R_k : group surface area parameter of group k
R : gas constant [KJ·mol^{-1}·K^{-1}]
T : temperature [K]
v_i : specific volume of component i [m^3/kg]
V_i : liquid molar volume of component i [m^3·kg^{-1} · mol^{-1}]
w_{ij} : interchange energy parameter of component i [KJ/mole]
X_{nom} : crosslinking ratio based on the assumption that the resulting network contains no dangling chain ends [-]
z : coordination number (typically z=10)

Greek Letters

ϕ_i : volume fraction of component i
$\Delta\mu_i$: chemical potential change of component i [KJ/Kg]
$\Delta\mu_{i, mix}$: chemical potential change due to mixing of component i [KJ/Kg]
$\Delta\mu_{i, el}$: chemical potential change due to elastic deformation of component i [KJ/Kg]
γ_i : activity coefficient of component i
$(\ln\gamma_i)^0$: portion of the log of the activity coefficient of component i
Γ_{ii} : non-random factor between component i−i
ν_i : group number of component i
ρ_i : densities of component i
θ_i : surface area fraction of component i

Superscript

0 : standard state

Subscripts

c : crosslinked
el : elastic deformation
i, j : component of binary systems
mix : mixing
nom : nominal
r : repeating

REFERENCES

Bell, C. L. and Peppas, N. A., "Equilibrium and Dynamic Swelling of Polyacrylates," *Polymer Eng. and Sci.*, **36**(14), 1856 (1996).

Brannon-Peppas, L. and Peppas, N. A., "Equilibrium Swelling Behavior of Ph Sensitive Hydrogels," *Chem.Eng. Sci.*, **46**, 715 (1991).

Brannon-Peppas, L. and Peppas, N. A., "Structural Analysis of Charged Polymeric Networks," *Polym. Bul.*, **20**, 285 (1988).

Buchholz, F. L. and Peppas. N. A., "Superabsorbent Polymer Science and Technology," *ACS Synposium.*, 206 (1993).

Chang, S. C., Yoo, J. S., Woo, J. W. and Choi, J. S., "Measurement and Calculation of Swelling Equilibria for Water/Poly(acrylamide-sodiumallylsulfonate) Systems," *Korean J. Chem. Eng.*, **16**, 581 (1999).

Choi, J. S., Tochigi, K. and Kojima, K., "Measurement and Correlation of Vapor-Liguid Equilibria in Polymer Solutions Containing Polystyrene with Polymer ASOG," *Fluid Phase Equilibria*, **111**, 143 (1995).

Flory, P. J., "Principles of Polymer Chemistry," Conell University Press, Ithaca, NY, London (1953).

Flory, P. J. and Rehner, J., "Statistical Mechanics of Cross-linked Polymer Networks," *J. Chem. Phys.*, **11**, 512 (1943a).

Flory, P. J. and Rehner, J., "Statistical Mechanics of Cross-linked Polymer Networks," *J. Chem. Phys.*, **11**, 521 (1943b).

Fredenslund, A., Jones, R. L. and Prausnitz, J. M., "Group Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixture," *AIChEJ.*, **21**(6), 1086 (1975).

Gmehling, J., Rasmussen, P. and Fredenslund, Aa., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 2," *Ind. Eng. Chem. Pro. Des. Dev.*, **32**, 118 (1982).

Guggenheim, E. A., "Mixtures," Clarendon Press, Oxford (1952).

Guggenheim, E. A., "Statistical Thermodynamics of Mixtures with Nonzero Energies of Mixing," *Proc. R. Soc. London*, **A183**, 213 (1944).

Gusler, G. M. and Cohen, Y., "Equilibrium Swelling of Highly Cross-Linked Polymeric Resin," *Ind. Eng. Chem. Res.*, **33**, 2345 (1994).

James, H. M. and Guth, E., "Theory of the Elastic Properties of Rubber," *J. Chem. Phys.*, **11**, 455 (1943).

Kim, S. J., Yoo J. S. and Choi, J. S., "Application of UNIFAC Model for Swelling Equilibria of Mixed Solvent/Poly(vinylchloride) Systems," *HWAHAK KONGHAK*, **36**, 314 (1998).

Kojima, K. and Tochigi, K., "Prediction of Vapor-Liquid Equilibria by ASOG Method," Elsevier, Amsterdam (1979).

Liu, Z. S. and Rempel, G. L., "Preparation of Superabsorbent Polymers by Crosslinking Acrylic Acid and Acrylamide Copolymers," *J. Appl. Polym. Sci.*, **64**, 1345 (1996).

Oishi, T. and Prausnitz, J. M., "Estimation of Solvent Activities in Polymer Solutions using a Group-Contribution," *Ind. Eng. Chem. Pro. Des. Dev.*, **17**, 333 (1978).

Panayiotou, C. and Vera, J. H., "The Quasi-Chemical Approach for Non-Randomness in Liquid Mixtures. Expressions for Local Compositions with an Application to Polymer Solutions," *Fluid Phase Equilibria*, **5**, 55 (1980).

Parks, L. R., U.S.Pat, 4295987 (1981).

Prange, M. M., Hooper, H. H. and Prausnitz, J. M, "Thermodynamics

of Aqueous Systems Containing Hydrophilic Polymers of Gels," *AIChE J.*, **35**, 803 (1989).

Stanley, F. W., Lamphere, J.C. and Chonde, Y., U.S.Pat, 4351261 (1987).

Tochigi, K., Tiegs, D., Gmehling, J. and Kojima, K., "Determination of New ASOG Parameters," *J. Chem. Eng. Japan*, **23**, 453 (1990).

Wall, F. T. and White, R. A., "A Distribution Function for Polymer Lengths," *Macromolecular*, **7**, 849 (1974).

Yamasaki, H. and Harada, S., U.S.Pat., 4446261 (1984).

Yao, K. J. and Zhou, W. J., "Synthesis and Water Absorbency of the Copolymer of Acrylamide with Anionic Monomers," *J. Appl. Polym. Sci.*, **53**, 1533 (1994).

Yoshida, T., Iwagami, S., Ueshima, T. and Hosoda, Y., U.S.Pat., 4351922 (1982).

Zhou, W. J., Yao, K. J. and Kurth, M. J., "Synthesis and Swelling Properties of the Copolymer of Acrylamide with Anionic Monomers," *J. Appl. Polym. Sci.*, **62**, 911 (1996).