Measurement and Calculation of Swelling Equilibria for Water/Poly(acrylamide-sodiumallylsulfonate) Systems

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Abstract–Superabsorbent poly(acrylamide-sodiumallylsulfonate) was synthesized from acrylamide (AM) and sodiumallylsulfonate (SAS) by a solution polymerization method. N,N'-methylenebisacrylamide (BIS) was used as the crosslinker; potassium persulfite (PP) and N,N,N',N'-tetra-methylenediamine (TMEDA) were used as the redox initiator during the synthesis. The absorption capacities of the synthesized superabsorbent poly(AM-SAS) were repeatedly measured to obtain the optimal poly(AM-SAS) according to the variations of monomer concentration at 298.15 K. Its maximal absorption capacity appeared as 811 times at 0.1 mol/L among from 0.01 mol/L to 0.16 mol/L of SAS concentrations. The swelling equilibria at those conditions from 298.15 K to 318.15 K were measured and used to estimate the parameters by correlating with the Flory-Huggins model. The swelling behavior could be described by the parameters and the calculated values agreed satisfactorily with the experimental data.

Key words : Superabsorbent Poly(AM-SAS), Solution Polymerization Method, Maximal Absorption Capacities, Flory-Huggins Model

INTRODUCTION

In everyday life, cottons, papers and sponges are commonly used to absorb water. These materials absorb only a few times water against their weights because they absorb the water with a capillary phenomenon and have the property that the absorbed waters are easily released under external pressure [Liu and Rempel, 1996]. New materials, which are called superabsorbent polymers, have been developed to apply to various industries by improving their properties. They absorb a few hundreds to thousands of times water and have the characteristic to keep the water in their network structure under external pressure. The superabsorbent polymers have broad uses for industrial applications such as sanitary materials, diapers, agriculture fields, medicines, and other advanced technologies.

Their development has continued to derivatives that have about a thousand times the absorption capacity. For example, Gugliemelli et al. [1969] synthesized the starch-acrylonitrile graft copolymer without a crosslinker and Fanta et al. [1978] also synthesized acrylic acid-starch which was a graft-copolymer by using either the Ce^{4+} ion or the Fe^{2+}/H_2O_2 as an initiatior. Yoshida et al. [1982] reported the results of superabsorbent polyacrylates obtained by polymerizing sodium acrylate which was the 16% aqueous solution in the presence of poly(ethylene glycol diglycidyl ether) and persulfate-triethanoamine as a crosslinker and an initiator, respectively. Parks [1981] prepared a superabsorbent polyacrylate by copolymerizing acrylic acid (AA) with the sodium persulfate as an initiator and 10% aqueous tetraethyleneglycol diacrylate solution accompanying with a functional divinyl group as a crosslinker at 60 °C. Yao and Zhou [1994] also synthesized the copolymers of acrylamide with anionic monomers and considered various properties of them. There was little research about calculation of swelling equilibria in spite of the many studies mentioned above. Park et al. [1994] reported the swelling behaviors of HSMA/PVA IPN gels in the mixed solvents and determined two adjustable parameters related to gel properties from the model based on Tanaka theory. They could also describe the phase transition of the gel in mixed solvents by their calculated results.

In this work, we prepared a poly(AM-SAS) to consider the swelling behavior of superabsorbent polymer. A poly(AM-SAS) was synthesized from AM and SAS and its optimal synthetic condition was suggested. The swelling equilibria of the polymer were measured for water (1)/poly(AM-SAS) (2) systems at 298.15 K to 313.15 K. The interaction energy parameters between the water and poly(AM-SAS) were estimated by correlating also swelling equilibrium data with the Flory-Huggins model [Flory, 1953; Gusler and Cohen, 1994]. The swelling behaviors were described and the calculated values compared with the experimental data.

EXPERIMENTAL

1. Materials

Acrylamide (Aldrich, USA) and sodium allylsulfonate were the special grade and used without further purification. N,N'-methylenebisacrylamide (BIS) (Aldrich, USA) was also used as purchased. The potassiumpersulfite (PP) and N,N,N',N'-tetramethylenediamine (TMEDA) (Sigma) were also used as same. The water was used after redistillation. Washing ethanol (first grade) was used as received.

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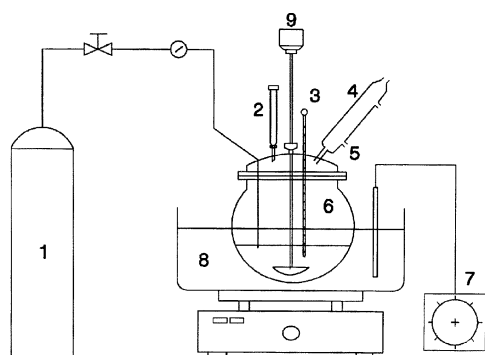E-mail : jschoi@daisy.kwangwoon.ac.kr

Fig. 1. Schematic diagram of synthesis apparatus.

1. Nitrogen bomb   6. 4-Necked kettle
2. Dropping funnel   7. Thermocontroller
3. Thermometer   8. Water bath
4. Coiled condenser   9. Mechanical stirrer
5. Cooling water

2. Synthesis Apparatus and Procedure

The synthesis apparatus was designed to synthesize a pure and high quality polymer product by constraining the purities during synthesis and shown on Fig. 1. The synthesis was carried out in nitrogen atmosphere to prevent an unnecessary reaction between monomers and oxygen during the total synthetic procedure. A stirrer was a mechanical teflon bar, and the constant water bath was equipped with a precise temperature controller (±0.01 K) to keep a constant temperature.

The synthesis was carried out in a 1 L flask equipped with a mechanical stirrer, condenser, and nitrogen bomb. The weighed monomers, initiator, and crosslinker were dissolved in distilled 200 ml water. The reaction medium was deaerated with the nitrogen while stirring for 20 min. The 0.1 N NaOH was added and an aqueous solution adjusted to pH 6. The crosslinked polymer was obtained after 2 h at 308.15 K. That was precipitated in ethanol, washed, and vacuum-dried overnight until constant weight was kept at 323.15 K. The product was milled and screened through a 60-mesh screen.

3. Swelling Measurement

The prepared poly(AM-SAS) powder was accurately weighed to 0.1 g and immersed in distilled water at each experimental temperature. The swollen poly(AM-SAS) was separated from the water by screening through a tared 60 mesh sieve and allowed to drain for 10 min. The sample was repeatedly reweighed at 10 min intervals until equilibrium approach.

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

$$\text{Absorption capacity} = \frac{\text{mass of water}}{\text{mass of dried polymer}} = \frac{m_2 - m_1}{m_1} \quad (1)$$

And volume fractions of poly(AM-SAS) for the water (1)/poly(AM-SAS) (2) systems on swelling equilibria were determined from Eq. (2).

$$\phi_i = \frac{\dfrac{m_i}{\rho_i}}{\sum\limits_j \dfrac{m_j}{\rho_j}} = \frac{v_i}{\sum\limits_j v_j} \quad (2)$$

Table 1. Densities of water and polymer measured

Material	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Water	0.997	0.996	0.994	0.992	0.990
Poly(AM-SAS)	0.750	0.750	0.750	0.750	0.750

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

Temp. (K)	ϕ_1	ϕ_2
298.15	0.9995	0.0005
303.15	0.9995	0.0005
308.15	0.9996	0.0004
313.15	0.9997	0.0003
318.15	0.9998	0.0002

The measured densities of each component to determine the volume fraction were shown in Table 1. Determined swelling equilibrum data were listed in Table 2.

RESULTS AND DISCUSSION

1. Optimal Absorption Capacity

It was essential that the optimal absorption capacity should be determined to obtain the optimal superabsorbent poly(AM-SAS) to absorb water. The concentrations of SAS were varied to do so, but that of AM, initiators (PP, TMEDA), and crosslinker (BIS) were fixed during the synthetic procedure. Each concentration was 0.97 mol/L for AM, 0.00267 mol/L for PP, 0.003 mol/L for TMEDA, and 0.0064 mol/L for BIS. Their synthesis conditions were similar to those of Yao and Zhou [1994] but had a different point of view from variations of monomer. The superabsorbent poly(AM-SAS) was synthesized according to the variations from 0.01 mol/L to 0.16 mol/L of SAS concentrations at 298.15 K. The results were shown in Fig. 2, and the
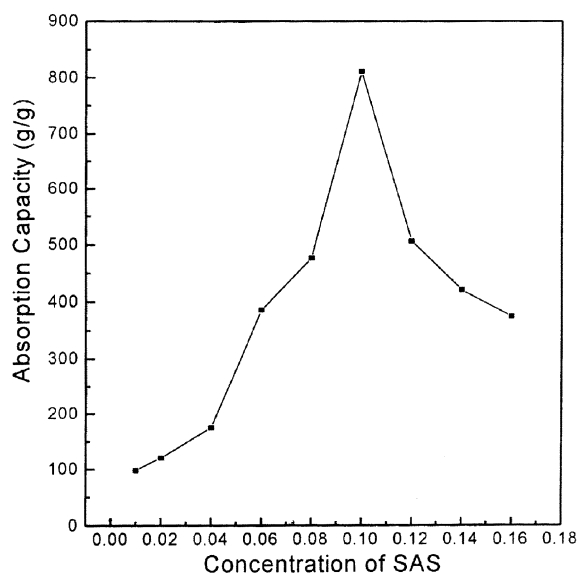

Fig. 2. Determination of optimal absorption capacities of poly(AM-SAS) at 298.15 K.
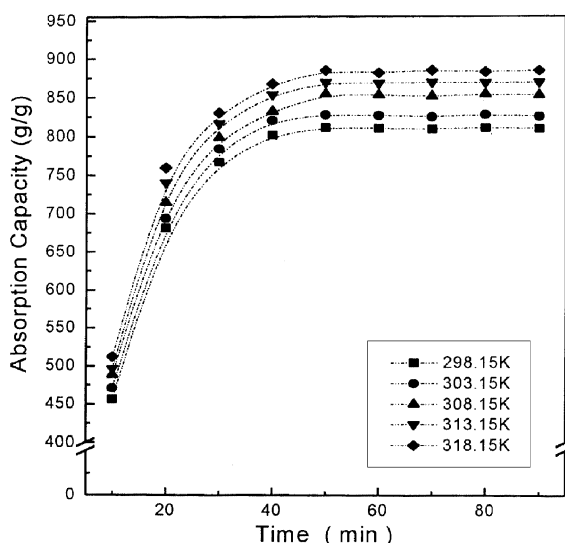
Fig. 3. Water absorption capacities of poly(AM-SAS) at 0.1 mol/ L of SAS.

absorption capacity of poly(AM-SAS) represented the optimal value when the concentration of SAS was 0.1 mol/L. The absorption capacities of superabsorbent polymer prepared from those synthesis conditions were improved in comparison with the result of Yao and Zhou [1994].

2. Temperature Effect on Absorption Capacity

Water absorption capacities of poly(AM-SAS) were again measured from 298.15 K to 318.15 K when the optimal concentration of SAS was 0.1 mol/L. Their results are shown in Fig. 3 and water absorption capacities of poly(AM-SAS) exhibited a tendency to increase from 811 to 885 times according to the increment of temperatures.

3. Calculation of Swelling Equilibria

The swelling equilibrium data of Table 2 were correlated with the swelling model to describe the swelling behavior of the superabsorbent poly(AM-SAS) in water. The swelling model [Flory, 1953] to express swelling equilibria consists of the sum of chemical potential changes of the solvent in the bulk phase and the elastic deformation of the polymer network. One term is due to mixing in the bulk phase and the other term due to elastic deformation induced by an expansion of network structure. Therefore, when the superabsorbent poly(AM-SAS) was swelled in the water at constant temperature and pressure, the swelling model was represented as follows:

$$\Delta\mu_i = \Delta\mu_{i,mix} + \Delta\mu_{i,el} = 0 \tag{2}$$

In this work, Flory-Huggins expression [Flory, 1953] was used to describe the chemical potential change due to of mixing. The expression for the water (1)/poly(AM-SAS) (2) systems was given as the next equation.

$$\Delta\mu_{i,mix} = RT[\ln\phi_i + (1-\phi_i) + \chi_i(1-\phi_i)] \tag{3}$$

The Wall and White [1974] expression was also used to describe the chemical potential change due to elastic deformation. It is given by

$$\Delta\mu_{i,el} = RT\left[\frac{V_i}{v_2 M_c}\left(1 - \frac{2M_c}{M}\right)\left(\frac{5}{3}\phi_2^{1/3} - \frac{7}{2}\phi_2\right)\right] \tag{4}$$

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). It led to $2M_c/M \ll 1$. The molecular weight between crosslinks, M_c, was determined using Eq. (5) [Bell and Peppas, 1996].

$$M_c = \frac{M_r}{nX_{nom}} \tag{5}$$

Here, M_r was the molecular weight of the repeating unit for the crosslinked polymer and is determined from the initial concentration ratios of AM and SAS. X_{nom} was used by the recommended value of Bell and Peppas [1996]. It was a typical value and $X_{nom}=0.001$. Therefore, M_c was evaluated from Eq. (5) and its value $M_c=43547.2$. It was fixed to estimate the Flory-Huggins interaction parameters during the calculation procedure. The computational procedures were described in detail in the work of Kim et al. [1998]. Their results are shown in Table 3. The interaction energy parameters between water and poly(AM-SAS), the polymeric network, were increased according to the temperature increments. That meant that these phenomena made the poly(AM-SAS) more swellable, and the polymeric network became more and more gelable by absorbing much water into the polymer as shown in the experiments. The calculated values agreed satisfactorily with the experimental data as shown in Table 3.

CONCLUSION

The superabsorbent poly(AM-SAS) was synthesized to describe its phase behavior at the optimal conditions with maximum absorption capacity. The optimal condition was obtained when the concentrations of SAS were 0.1 mol/L at 298.15 K. The swelling equilibria of poly(AM-SAS) prepared on those optimal conditions were measured in water at the experimental temperature. Their values were converted to the volume fractions and appeared as from 811 to 885 times against the dried poly(AM-SAS). They were correlated with the Flory-Rehner equation to estimate the interaction parameters. The estimated interaction parameters increased according to the increment of temperature and proved that the swelling behavior between water and poly (AM-SAS) may become more and more gelable. The average deviations between the calculated and experimental values agreed within below 0.0033% for water (1)/poly(AM-SAS) (2) systems.

Table 3. Flory-Huggins interaction parameters and average deviations for water (1)/poly(AM-SAS) (2) systems

Temp. (K)	χ_1	Ave. dev (%)
298.15	1151.1	0.0033
303.15	1175.5	0.0033
308.15	1212.2	0.0032
313.15	1234.5	0.0031
318.15	1257.4	0.0030
Average		0.0032

Average deviation $(\%) = \frac{1}{N}\sum_i\left(\frac{|\phi_{1,cal,i} - \phi_{1,exp,i}|}{\phi_{1,exp,i}}\right)$

NOMENCLATURE

M   : molecular weight of the crosslinked polymer
M_c : average molecular weight of the chain between cross-
         linked polymer [Kg/mol]
M_r : molecular weight of the repeating unit for the cross-
         linked polymer [Kg/mol]
n_i : number of moles component i
n   : number of functional sites for crosslinking agent [-]
R   : gas constant [KJ·mol^{-1}·K^{-1}]
T   : temperature [K]
v_i : specific volume of component i [m^3/Kg]
X_{nom} : crosslinking ratio based on the assumption that the re-
         sulting network contains no dangling chain ends [-]

Greek Letters

ϕ_i : volume fraction of component i
χ_i : Flory-Huggins interaction parameter
$\Delta\mu_{i,\,mix}$: chemical potential changes due to mixing [KJ/Kg]
$\Delta\mu_{i,el}$: chemical potential changes due to elastic deformation
         [KJ/Kg]

Subscripts

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

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