

Thermodynamic Correlation of Partial and Saturation Swelling of Styrene–Acrylonitrile Copolymer Particles by Styrene and Acrylonitrile Monomers

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ABSTRACT: The possibility of thermodynamic correlation of partial and saturation swelling of styrene–acrylonitrile (SAN) copolymer particles by styrene (St) and acrylonitrile (AN) monomers is investigated. The unknown Flory–Huggins interaction parameters involved in the thermodynamic swelling equations are estimated by fitting the equations to the experimentally observed monomer concentrations. It is shown that the concentration of each monomer in SAN copolymer particles predicted by using the thermodynamic swelling equations with the parameters and constants estimated in this study agrees fairly well with that observed experimentally over a wide range of experimental conditions. The validity and utility of the parameters and constants estimated from saturation swelling are also demonstrated by showing that the experimental results for partial swelling of SAN copolymer particles by AN monomer dissolved in the aqueous phase agree with those predicted by the thermodynamic equation for partial swelling. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 931–939, 1997

Key words: swelling of polymer particles; monomer partitioning; styrene; acrylonitrile

INTRODUCTION

It is important that the concentration of each monomer in copolymer particles can be predicted during the course of emulsion copolymerization because they determine the rate of emulsion copolymerization, the composition of copolymer produced, monomer–polymer compatibility, and so on. Corresponding to the three intervals from the beginning to the end of emulsion copolymerization, saturation swelling of copolymer particles by each monomer takes place in so-called intervals I and II, where monomer droplets exist in the continuous aqueous phase; whereas partial swelling of copolymer particles occurs in interval III, where separate monomer droplets no longer exist in the

continuous aqueous phase because they have been already absorbed into both the copolymer particles and aqueous phase.

There are generally two methods for predicting the monomer concentration in copolymer particles in emulsion copolymerization systems. One is the empirical method,^{1,2} where the saturation concentration of each monomer in the copolymer particles is correlated by empirical equations as a function of the comonomer composition in the separate monomer droplet phase and the copolymer composition in the copolymer particles. The other is the thermodynamic approach,^{3–11} where it is generally recognized that the monomer partitioning among three phases constituting an emulsion polymerization system is governed by a thermodynamic equilibrium, which is quickly reached and maintained during the course of emulsion copolymerization because of rapid monomer diffusion among these phases. In order to deeply under-

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stand the swelling behavior of polymer particles by monomer, the thermodynamic approach appears to be the most promising method. In the early stage, Morton et al.³ successfully applied the thermodynamic approach to the prediction of saturation swelling of polymer particles by monomers. In the last few years, the quantitative model proposed by Morton et al.³ has been extended by Ugelstad et al.,⁴ Guillot,⁵ and Tseng et al.⁶ to describe the saturation swelling of latex particles by two monomers. The partial swelling of latex particles, which has received less attention to date, has also been studied by Vanzo et al.,⁷ Gardon,⁸ and Maxwell et al.^{9,10}

In the emulsion copolymerization of styrene (St) and acrylonitrile (AN), the thermodynamic approach has been applied by Guillot et al.^{5,11} for predicting the equilibrium swelling behavior of styrene–acrylonitrile (SAN) copolymer particles by a St and AN monomer mixture. Although they claimed that the thermodynamic approach could be applied successfully to this copolymerization system, they did not give the Flory–Huggins polymer–monomer interaction parameters and other constants used in their calculation. Moreover, they have not thoroughly demonstrated the validity of the thermodynamic approach by comparing the observed equilibrium swelling data with theoretical predictions over a wide range of St and AN mole ratio in the monomer feed and of the copolymer composition in SAN copolymer particles.

In this article, we examine the possibility of thermodynamic correlation of partial and saturation swelling of SAN copolymer particles by St and AN monomers. In the present stage, however, there is still difficulty in applying the thermodynamic approach to the St–AN emulsion copolymerization system because (1) no reliable methods are available for calculating the interaction parameters in this system, and (2) it is almost impossible to measure the interaction parameter between AN monomer and polyacrylonitrile (PAN) $\chi_{A,PA}$ by saturation experiments because AN monomer and PAN are almost immiscible. In this article, therefore, the interaction parameters are experimentally determined so that they can explain the extensive and systematic experimental data on the saturation swelling of SAN copolymer particles by a St and AN monomer mixture reported in our previous article.² In order to demonstrate the validity and utility of the interaction parameters thus determined, the experimental results for partial swelling of SAN copolymer par-

ticles are also compared with those predicted by applying these interaction parameters to the thermodynamic equations for partial swelling.

EXPERIMENTAL

The experimental method for saturation swelling was the same as that employed in the previous article.² Therefore, only the experimental procedure for partial swelling is exclusively described here. The concentrations of St and AN monomers in SAN copolymer particles, which are in equilibrium with those in the aqueous phase in the absence of a separate monomer droplet phase, were measured by the following procedure. The latex samples containing SAN copolymer particles saturated with a St and AN monomer mixture or AN monomer alone were obtained firstly by equilibrating unswollen SAN copolymer latex samples in the presence of a monomer droplet phase and then separating the remaining monomer droplets by centrifugation. A small amount of this latex sample at saturation swelling was mixed with a given amount of an unswollen SAN copolymer latex sample with the same solid content and copolymer composition. The mixture was transferred into a 100 cm³ flask and was gently agitated for 4 h at 50°C to attain equilibrium. A small quantity of this sample was withdrawn by a syringe and poured into excess methanol to precipitate SAN copolymer after weighing the sample. The precipitated SAN copolymer was filtered off with a glass crucible and was weighed after complete dryness in an oven to determine the total weight of copolymer contained in the sample. The monomer concentration in the filtrate was also measured by gas chromatography (GC) to determine the total amount of St and AN monomers contained in the sample. On the other hand, the residual sample was immediately subjected to ultracentrifugation at 35,000 rpm for 2.5 h for separating the monomer-swollen SAN copolymer particles from the aqueous phase, then the concentration of each monomer in the serum was determined by GC. From these data and with the same equations and assumptions described in the previous article,² we calculated the concentrations of St and AN monomers in SAN copolymer particles, $[M_S]_p$ and $[M_A]_p$, and in the aqueous phase, $[M_S]_w$ and $[M_A]_w$, which are in equilibrium with those in SAN copolymer particles.

EXPERIMENTAL RESULTS AND DISCUSSION

Saturation Swelling

Thermodynamic Equations

At equilibrium, the partial molar free energy of i monomer in SAN copolymer particles must be equal to that in the monomer droplets, as shown by

$$\left(\frac{\Delta G}{RT}\right)_i^p = \left(\frac{\Delta G}{RT}\right)_i^d \quad (1)$$

where superscripts p and d refer to the copolymer particle and the monomer droplet, respectively. According to Ugelstad et al.,⁴ the partial molar free energies for St and AN monomers in the copolymer particles and the monomer droplets can be expressed by the following equations, respectively.

$$\begin{aligned} \left(\frac{\Delta G}{RT}\right)_S^p = & \ln \Phi_{SP} + (1 - m_{SA})\Phi_{AP} + \Phi_P + \chi_{SA}\Phi_{AP}^2 \\ & + \chi_{SP}\Phi_P^2 + \Phi_{AP}\Phi_P(\chi_{SA} + \chi_{SP} - \chi_{AP}m_{SA}) \\ & + \frac{2\bar{V}_S\gamma\Phi_P^{1/3}}{R_pRT} \quad (2) \end{aligned}$$

$$\begin{aligned} \left(\frac{\Delta G}{RT}\right)_A^p = & \ln \Phi_{AP} + (1 - m_{AS})\Phi_{SP} + \Phi_P + \chi_{SA}\Phi_{SP}^2 \\ & + \chi_{AP}\Phi_P^2 + \Phi_{SP}\Phi_P(\chi_{SA} + \chi_{AP} - \chi_{SP}m_{AS}) \\ & + \frac{2\bar{V}_A\gamma\Phi_P^{1/3}}{R_pRT} \quad (3) \end{aligned}$$

$$\left(\frac{\Delta G}{RT}\right)_S^d = \ln \Phi_{Sd} + (1 - m_{SA})\Phi_{Ad} + \chi_{SA}\Phi_{Ad}^2 \quad (4)$$

$$\left(\frac{\Delta G}{RT}\right)_A^d = \ln \Phi_{Ad} + (1 - m_{SA})\Phi_{Sd} + \chi_{SA}\Phi_{Sd}^2 \quad (5)$$

On the other hand, the material balance on the monomer-swollen copolymer particles and on the monomer droplets is given, respectively, by

$$\Phi_{SP} + \Phi_{AP} + \Phi_P = 1, \quad \Phi_{Sd} + \Phi_{Ad} = 1 \quad (6)$$

where \bar{V}_A and \bar{V}_S are the molar volumes of AN and St monomers, respectively; R is the gas constant; T is the temperature, R_p is the unswollen radius of the particle, γ is the interfacial tension

between the particle and aqueous phases; m_{AS} is the ratio of the molar volume of AN monomer to that of the St monomer; χ_{SA} , χ_{SP} , and χ_{AP} are the interaction parameters between the St and AN monomers, the St and SAN copolymer, and the AN and SAN copolymer, respectively; Φ_{Ad} and Φ_{Sd} are the volume fractions of AN and St monomers in the monomer droplets, respectively; and Φ_{AP} , Φ_{SP} , and Φ_P are the volume fractions of the AN monomer, St monomer, and SAN copolymer in the monomer-swollen SAN copolymer particles, respectively.

Strictly speaking, eqs. (4) and (5) should include the interfacial energy terms, as shown in eqs. (2) and (3). However, the diameter of a monomer droplet is, in general, much larger than that of a polymer particle; hence, the corresponding interfacial energy terms can be safely neglected in eqs. (4) and (5).¹⁰ Considering eq. (1), we obtain three simultaneous equations from eqs. (2)–(6), which involve two nonlinear and one linear algebraic equations with three unknown variables, Φ_{AP} , Φ_{SP} , and Φ_P , to describe the saturation swelling of the system. Thus, the solution of these three simultaneous equations to Φ_{AP} and Φ_{SP} at given value of Φ_{Ad} provides the concentration of each monomer in the monomer-swollen copolymer particles as a function of Φ_{Ad} with the aid of the following equations.

$$[M_S]_p = \frac{\Phi_{SP}\rho_S^m}{M_S} \quad (7)$$

$$[M_A]_p = \frac{\Phi_{AP}\rho_A^m}{M_A} \quad (8)$$

where $[M_S]_p$ and $[M_A]_p$ are the concentrations of St and AN monomers in the monomer-swollen SAN copolymer particles, respectively; M_S and M_A are the molecular weights of St and AN monomers, respectively; and ρ_S^m and ρ_A^m are the densities of St and AN monomers, respectively.

It must be noted here that the values of the parameters γ , χ_{SP} , and χ_{AP} are unknown at the present stage. In order for the concentration of each monomer in the monomer-swollen SAN copolymer particles to be expressed as a function of Φ_{Ad} by solving eqs. (1) and (6) for Φ_{AP} and Φ_{SP} , we have to determine these three unknown constants first.

Determination of the Values of the Parameters γ , χ_{SP} , and χ_{AP} and Their Applicability

In place of the monomer-swollen SAN copolymer particle–water interfacial tension, γ , the value of

Table I Influence of NaLS Concentration on the Monomer–Water Interfacial Tension (25°C)

NaLS (g/dm ³)	0	1.2	2.4	4.3
γ (mN/m)	16.9	9.5	8.7	8.2

the monomer–water interfacial tension was employed as a first approximation because of the difficulty in measuring it. We measured the monomer–water interfacial tension with a Du–Noüy tensiometer, as employed by Tseng et al.⁶ Table I shows the monomer–water interfacial tension measured at 25°C with varying sodium lauryl sulfate (NaLS) concentration in the water phase. The value of 8.0 mN/m near the experimental condition in this study (NaLS = 6.25 g/dm³ water) was chosen.

Next, let's explain how to determine the values of the monomer–copolymer interaction parameters, χ_{SP} and χ_{AP} . In this study, we also assumed that the monomer–copolymer interaction parameters can be expressed as a volumetric mean of the monomer–homopolymer interaction parameters, as shown below.¹¹

$$\chi_{SP} = (1 - y_A)\chi_{S,PS} + y_A\chi_{S,PA} \quad (9)$$

$$\chi_{AP} = y_A\chi_{A,PA} + (1 - y_A)\chi_{A,PS} \quad (10)$$

where $\chi_{S,PS}$, $\chi_{S,PA}$, $\chi_{A,PS}$, and $\chi_{A,PA}$ are the interaction parameters of St monomer–PSt, of St monomer–PAN, of AN monomer–PSt, and of AN monomer–PAN, respectively; and y_A represents the volume fraction of AN monomer units in SAN copolymer.

According to Guillot's approach,¹¹ one may directly predict the monomer–polymer interaction parameters from the solubility parameter δ . It is certainly known that the following equation works well when the solubility parameters for monomer and polymer are very close to each other and the monomer and polymer are both nonpolar like the St monomer–PSt pair, namely, a completely miscible solvent–solute pair.¹²

$$\chi = 0.34 + \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \quad (11)$$

where V_1 is the molar volume of monomer, and δ_1 and δ_2 are the solubility parameters for monomer and polymer, respectively. Equation (11) predicts the value of $\chi_{S,PS} = 0.395$, which is very close to an experimentally determined value of $\chi_{S,PS}$

= 0.4.⁶ However, it is difficult to apply eq. (11) to the system consisting of SAN copolymer particles swollen with a St and AN monomer mixture. This is due to the fact that this system contains the interaction parameters for both polar and nonpolar species, such as $\chi_{A,PA}$, $\chi_{A,PS}$, and $\chi_{S,PA}$. For polar systems, especially for a completely immiscible monomer–polymer pair like AN monomer–PAN, there are still no good ways to predict the value of the Flory's interaction parameter with reasonable accuracy,¹² although several solution theories^{13,14} and an estimation method for polar molecules¹⁵ have been proposed to date.

In order to overcome this key problem in this study, the values of $\chi_{A,PA}$, $\chi_{A,PS}$, and $\chi_{S,PA}$ were experimentally estimated as follows: To begin with, we determined the best values of χ_{SP} and χ_{AP} , with the aid of the nonlinear least-squares method, with which eqs. (1)–(6) could explain the experimental relationship between the saturation concentrations of St and AN monomers in the monomer-swollen SAN copolymer particles, $[M_S]_P$ and $[M_A]_P$, and the weight fraction of AN monomer in the monomer droplets, F_{Ad} , for SAN copolymer particles with $H_A = 0.3$ and 0.8 ($F_{Ad} = (\rho_A^m \Phi_{Ad} / \rho_A^m \Phi_{Ad} + \rho_S^m (1 - \Phi_{Ad}))$; and H_A is the weight fraction of AN monomer units in SAN copolymer particles.² Figures 1 and 2 show the reported experimental data¹ for the saturation swelling of SAN copolymer particles with different copolymer composition, $H_A = 0.1$ – 0.8 , as a function of F_{Ad} . As shown by the solid lines in Figure 1, it was found that the values of $\chi_{SP} = 0.73$ and $\chi_{AP} = 0.55$ could best explain the experimental data for SAN copolymer particles with $H_A = 0.3$. Introduction of the values of $\chi_{SP} = 0.73$ and $\chi_{AP} = 0.55$ thus determined into eqs. (9) and (10), with the assumption of volume additivity for PSt and PAN in calculating the value of y_A , gives the following equations:

$$\left(\frac{0.7\rho_A}{0.3\rho_S + 0.7\rho_A} \right) \chi_{S,PS} + \left(\frac{0.3\rho_S}{0.3\rho_S + 0.7\rho_A} \right) \chi_{S,PA} = 0.73 \quad (12)$$

$$\left(\frac{0.7\rho_A}{0.3\rho_S + 0.7\rho_A} \right) \chi_{A,PS} + \left(\frac{0.3\rho_S}{0.3\rho_S + 0.7\rho_A} \right) \chi_{A,PA} = 0.55 \quad (13)$$

where ρ_A and ρ_S are the densities of PSt and PAN, respectively. Then, we can obtain the value of

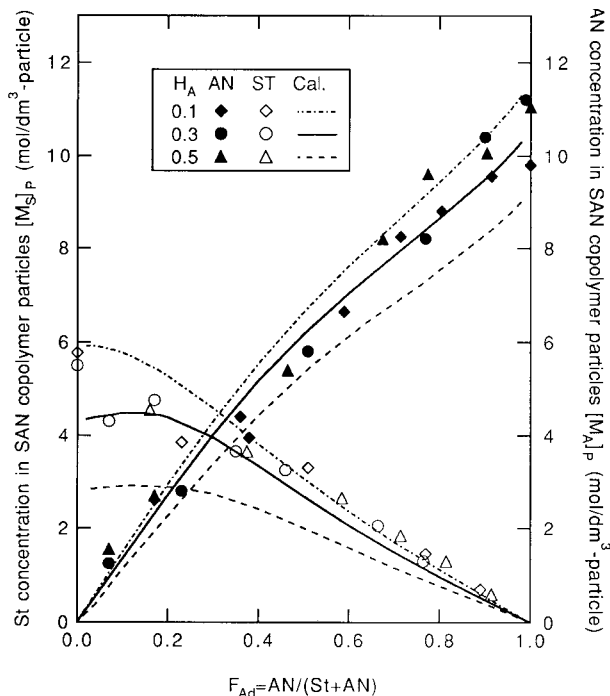


Figure 1 Comparison between the experimental and predicted saturation concentrations of St and AN monomers in the monomer-swollen SAN polymer particles as a function of the weight fraction of AN monomer in a separate comonomer droplet with varying the copolymer composition in SAN copolymer particles, H_A (50°C; $H_A = 0.1, 0.3$, and 0.5).

$\chi_{S,PA} = 1.58$ from eq. (12), when the literature value of $\chi_{S,PS} = 0.40$ is employed.⁶ Introduction of the value of $\chi_{S,PA} = 1.58$ thus obtained and $\chi_{S,PS} = 0.40$ into eq. (9) gives the value of $\chi_{SP} = 1.3$ for the condition of $H_A = 0.8$. Further, using the value of $\chi_{SP} = 1.3$ thus determined, we searched for the best value of χ_{AP} , which explains the experimental data for $H_A = 0.8$, and found the value of $\chi_{AP} = 0.79$. The solid lines in Figure 2 show the calculated results when the values of $\chi_{S,PA} = 1.58$ and $\chi_{AP} = 0.79$ are applied. Introduction of $\chi_{AP} = 0.79$ thus obtained for the experimental data for $H_A = 0.8$ into eq. (10) yields

$$\left(\frac{0.2\rho_A}{0.2\rho_A + 0.8\rho_S} \right) \chi_{A,PS} + \left(\frac{0.8\rho_S}{0.2\rho_A + 0.8\rho_S} \right) \chi_{A,PA} = 0.79 \quad (14)$$

Then, by solving the simultaneous equations, eqs. (13) and (14), we could obtain the values of $\chi_{A,PA} = 0.88$ and $\chi_{A,PS} = 0.42$, respectively. Thus, all the unknown parameters, $\chi_{S,PS}$, $\chi_{A,PA}$, $\chi_{A,PS}$,

$\chi_{S,PA}$, and γ , were determined and listed in Table II with other constants employed in this study.

In order to check the applicability of the parameters and constants listed in Table II, we compared the monomer concentrations in the polymer particles observed experimentally with those predicted by using eqs. (1)–(10) and the parameters and constants listed in Table II in Figures 1 and 2, respectively. It is seen that the concentrations of AN monomer predicted by thermodynamic equations agree, within an approximately 10% error, with those observed experimentally over the range $H_A = 0.1$ – 0.8 . In comparison with AN monomer, however, agreement is not necessarily so good for St monomer in the range $H_A = 0.3$ – 0.6 , especially in the lower range of F_{Ad} . The reason for this is not clear at the present stage, but the change of water–particle interfacial tension γ with H_A and F_{Ad} may be one possible reason. Furthermore, eqs. (9) and (10) may not necessarily be good approximations over the entire range of H_A . In the case of the unseeded emulsion copolymerization of St and AN, the applicability of the

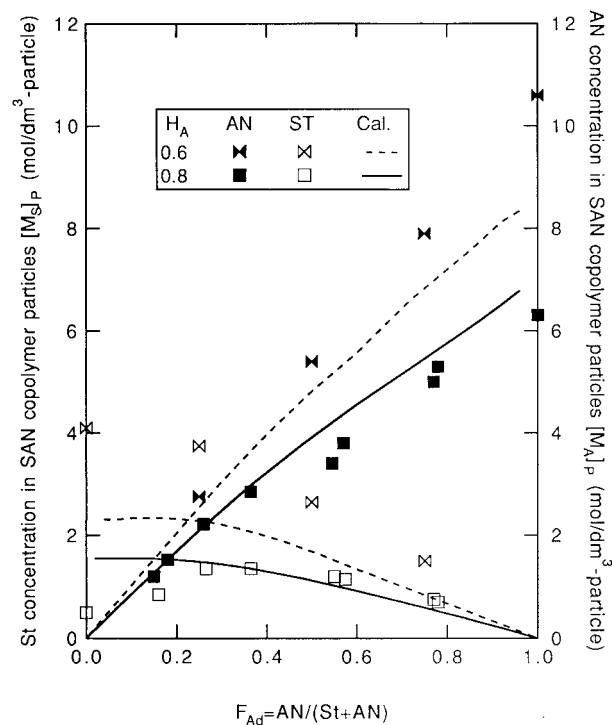


Figure 2 Comparison between the experimental and predicted saturation concentrations of St and AN monomers in the monomer-swollen SAN polymer particles as a function of the weight fraction of the AN monomer in a separate comonomer droplet with varying the copolymer composition in SAN copolymer particles, H_A (50°C; $H_A = 0.6$ and 0.8).

Table II The Values of the Parameters and Constants Determined or Used in This Study (50°C)

$\chi_{A,PA}, \chi_{A,PS}, \chi_{S,PA}, \chi_{S,PS}$	0.88	0.42	1.58	0.40
χ_{SA}, χ_{AW}	0.40	2.39 ^a		
m_{SA}, m_{AS}, m_{AW}	1.74	0.57	0.50 ^a	
γ (mN/m), $[M_A]_{aq,sat}$ (mol/dm ³)	8.0	1.40 ^a		
$\rho_A, \rho_B, \rho_A^m, \rho_B^m$ (g/cm ³)	1.08	1.05	0.806	0.902

^aFrom ref. 4.

thermodynamic correlation with much better accuracy is evident because the composition of copolymer developed in SAN copolymer particles H_A is not so different with the comonomer composition in the monomer feed F_{Ad} , where disagreement between the predicted and experimental values of the monomer concentrations is within experimental error. However, it will be reported in a succeeding article that even in the seeded emulsion copolymerization of St and AN, the thermodynamic correlation and the parameters and constants determined in this study can be applied with reasonable accuracy to the prediction of the monomer concentration in SAN copolymer particles.

Partial Swelling

Partial Swelling of SAN Copolymer Particles by St and AN Monomers Dissolved in Water

In order to examine whether the parameters and constants listed in Table II are valid and applicable to the prediction of partial swelling of SAN copolymer particles by St and AN monomers dissolved in the aqueous phase, the monomer concentrations in the SAN copolymer particles predicted by thermodynamic equations for partial swelling are compared with those observed experimentally.

For example, the partial molar free energy of AN monomer in the aqueous phase is approximately given by^{9,10}

$$\left(\frac{\Delta G}{RT}\right)_A^{aq} = \ln\left(\frac{[M]_{aq}}{[M]_{aq,Sat}}\right) \quad (15)$$

where $[M_A]_{aq}$ is the concentration of AN monomer in the aqueous phase and $[M_A]_{aq,sat}$ is the saturation concentration of AN monomer in the aqueous phase.

Partial swelling takes place in the absence of monomer droplets so that the following equation holds, for example, for AN monomer at equilib-

rium between the SAN copolymer particle and aqueous phases.

$$\left(\frac{\Delta G}{RT}\right)_A^P = \left(\frac{\Delta G}{RT}\right)_A^{aq} \quad (16)$$

In order to demonstrate the validity of eq. (16), the values of $\left(\frac{\Delta G}{RT}\right)_A^P$ and $\left(\frac{\Delta G}{RT}\right)_A^{aq}$ were calculated by introducing the parameters and constants listed in Table II, and the experimental values of $[M_A]_p$, $[M_S]_p$, and $[M_A]_{aq}$ listed in Table III, into eqs. (3) and (15) and were compared according to eq. (16) in Figure 3. In calculation, for example, $[M_S]_p$ was converted to Φ_{SP} by eq. (7). The solid line in the figure represents the case in which eq. (16) holds exactly. It is seen that the calculated values, at least in the range $H_A = 0.3$ – 0.8 , fall almost on the solid line, although the data points

Table III The Observed Partial Swelling Equilibria of St and AN Monomers Between the SAN Copolymer Particle and Aqueous Phases^a

H_A	$[M_A]_p$ [mol/dm ³]	$[M_S]_p$ [mol/dm ³]	$[M_A]_{aq}$ [mol/dm ³]
0.3	1.74	0.64	0.79
0.3	1.88	2.12	0.42
0.3	2.34	0.93	0.83
0.3	2.44	2.35	0.47
0.3	2.88	0.82	0.68
0.3	4.18	3.23	0.74
0.3	5.16	1.15	1.0
0.3	6.89	1.21	1.06
0.5	0.39	0.66	0.42
0.5	1.62	1.54	0.74
0.5	1.85	1.82	0.83
0.8	2.06	0.80	0.58
0.8	2.54	0.96	0.70

^a $[M_S]_{aq}$ was too small to measure. Swelling temperature: 25°C. Average diameter of SAN copolymer particles: $d_p = 100 \pm 20$ nm. Equilibration time: 4 h.

scatter somewhat around the theoretical line. Therefore, we can conclude from Figure 3 that eqs. (3), (15), and (16) and the parameters and constants listed in Table II can explain partial swelling of SAN copolymer particles by St and AN monomers dissolved in the aqueous phase within experimental error. Moreover, this also demonstrates that Henry's law is approximately applicable to calculate the partial molar free energy of AN monomer in the aqueous phase even for a latex system.⁷

Partial Swelling of SAN Copolymer Particles by AN Monomer Alone

In the emulsion copolymerization of St and AN, it sometimes happens that after complete polymerization of St monomer, residual AN monomer is still present in the reaction system, being partitioned between the resultant SAN copolymer particles and the aqueous phase. Therefore, it is important from practical purpose that one can predict the partition of AN monomer between SAN copolymer particles and the aqueous phase.

Considering eqs. (15) and (16), one can obtain the following equation for partial swelling of SAN copolymer particles by AN monomer dissolved in the aqueous phase,

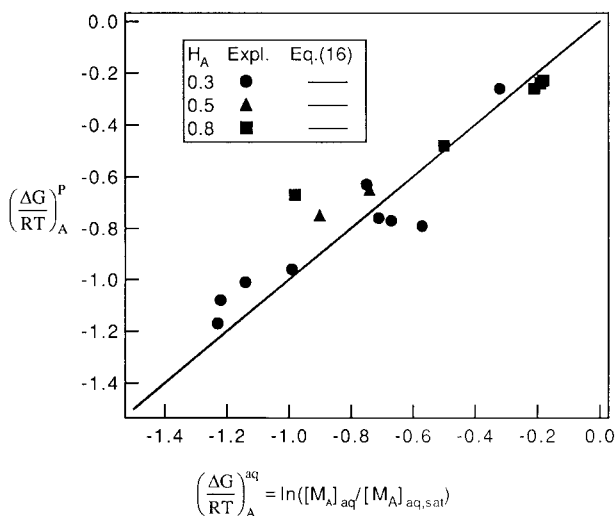


Figure 3 Experimental demonstration of the validity of eq. (16) by using SAN copolymer particles with $H_A = 0.3, 0.5$, and 0.8 at 25°C (solid line shows $\left(\frac{\Delta G}{RT}\right)_A^P = \left(\frac{\Delta G}{RT}\right)_A^{\text{aq}}$).

$$\ln \Phi_{AP} + \Phi_P \left(1 - \frac{1}{\bar{P}_n}\right) + \chi_{AP} \Phi_P^2 + \frac{2\bar{V}_A \gamma \Phi_P^{1/3}}{R_P R T} = \ln \left(\frac{[M]_{\text{aq}}}{[M]_{\text{aq,sat}}} \right) \quad (17)$$

where \bar{P}_n is the number average degree of polymerization, and the term $1/\bar{P}_n$ is usually negligible. This equation is called the Vanzo Equation.^{7,8} We have already demonstrated in the preceding section that eqs. (3) and (16), which is similar to eq. (17), is approximately valid for predicting partial swelling of SAN copolymer particles by St and AN monomers dissolved in the aqueous phase.

On the other hand, the partial molar free energy of AN monomer in the aqueous phase is alternatively given by⁴

$$\left(\frac{\Delta G}{RT}\right)_A^{\text{aq}} = \ln \Phi_{AW} + (1 - m_{AW})\Phi_W + \chi_{AW}\Phi_W^2 \quad (18)$$

where χ_{AW} is the AN monomer–water interaction parameter, and Φ_W and Φ_{AW} are the volume fractions of water and AN monomer in the aqueous phase, respectively, and satisfy $\Phi_{AW} + \Phi_W = 1$. The literature values of χ_{AW} and m_{AW} are also listed in Table II.⁴ Considering eq. (18), one can obtain the following equation alternative to eq. (17).

$$\ln \Phi_{AP} + \Phi_P \left(1 - \frac{1}{\bar{P}_n}\right) + \chi_{AP} \Phi_P^2 + \frac{2\bar{V}_A \gamma \Phi_P^{1/3}}{R_P R T} = \ln \Phi_{AW} + (1 - m_{AW})\Phi_W + \chi_{AW}\Phi_W^2 \quad (19)$$

Equations (17) and (19) can both provide the theoretical relationship between $[M_A]_P$ and $\frac{[M_A]_{\text{aq}}}{[M_A]_{\text{aq,sat}}}$ because $[M_A]_P = \frac{\Phi_{AP} \rho_A^m}{M_A}$ and Φ_{AW} can be converted to $\frac{[M_A]_{\text{aq}}}{[M_A]_{\text{aq,sat}}}$ by the following equation:

$$\frac{[M_A]_{\text{aq}}}{[M_A]_{\text{aq,sat}}} = \frac{\Phi_{AW} \rho_A^m}{M_A [M_A]_{\text{aq,sat}}} \quad (20)$$

where M_A is the molecular weight of AN monomer, and ρ_A^m is the density of AN monomer.

Let's compare the experimental and predicted relationship between $[M_A]_P$ and $\frac{[M_A]_{\text{aq}}}{[M_A]_{\text{aq,sat}}}$ to ex-

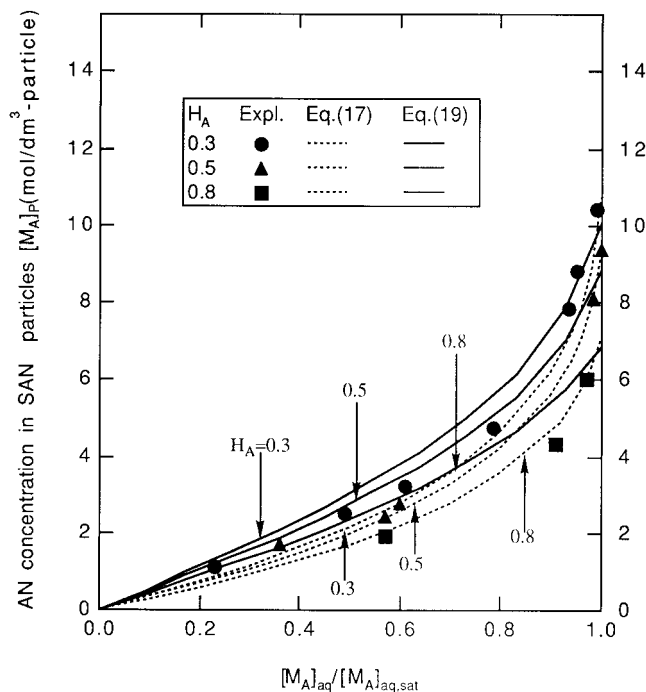


Figure 4 Comparison of the experimental and predicted relationship between $[M_A]_p$ and $\frac{[M_A]_{aq}}{[M_A]_{aq,sat}}$ for SAN copolymer particles with $H_A = 0.3, 0.5$, and 0.8 at 25°C .

amine which equation gives a much better prediction of the concentration of AN monomer in SAN copolymer particles. The experimental and predicted relationships between $[M_A]_p$ and $\frac{[M_A]_{aq}}{[M_A]_{aq,sat}}$ are compared in Figure 4, where experimental results for partial swelling of SAN latex particles with three different copolymer compositions (H_A) are presented. The solid lines show the theoretical values predicted by eq. (19), and the dotted lines are those predicted by eq. (17), respectively. It seems that the experimental data are explained somewhat better by eq. (17) than by eq. (19), although agreement depends on the literature values of χ_{AW} and m_{AW} used in eq. (19). Good agreement between the predicted and experimental values demonstrates further the validity of the interaction parameters $\chi_{A,PA}$, $\chi_{A,PS}$ determined from swelling experiments in this study. Furthermore, it is apparent from Figures 1, 2, and 4 that the copolymer composition in SAN copolymer particles, H_A , has a much weaker effect on partial swelling than on saturation swelling. The experimental results in Figure 4 clearly show that SAN copolymer particles can comparatively be swelled by the AN monomer, especially when the concentration of the AN monomer in the aqueous

phase is in the vicinity of its saturation concentration. This finding is different from the conclusion given by Guillot,⁵ who states that SAN copolymer particles are not practically swelled by the AN monomer in the absence of the St monomer inside the particles. However, the concentration of AN monomer in SAN copolymer particles decreases very rapidly with decreasing the concentration of AN monomer in the aqueous phase. This will be the main reason for the difficulty of attaining complete polymerization of residual AN monomer in the aqueous phase, which is often encountered in the emulsion copolymerization of St and AN.

CONCLUSION

In order to examine the possibility of thermodynamic correlation of partial and saturation swelling of SAN copolymer particles by St and AN monomers, we determined three unknown Flory–Huggins interaction parameters between the monomer and homopolymer, $\chi_{A,PA}$, $\chi_{A,PS}$, and $\chi_{S,PA}$, by fitting the thermodynamic equations for saturation swelling to the experimentally observed monomer concentrations in SAN copolymer particles. It was found that the predicted AN monomer concentra-

tions agree fairly well with those observed experimentally over a wide range of the copolymer composition in SAN copolymer particles, but the agreement between the predicted and observed St monomer concentration was somewhat worse compared to that for the AN monomer concentration.

Moreover, the experimental results for partial swelling of SAN copolymer particles by AN monomer in the aqueous phase were compared with those predicted by the thermodynamic equations in order to demonstrate the validity and utility of the parameters and constants determined from saturation swelling experiments. It was shown from this comparison that these parameters and constants and the thermodynamic equations for partial swelling could also be applied to the prediction of partial swelling with reasonable accuracy.

It will be reported in a succeeding article that in the seeded emulsion copolymerization of St and AN with SAN seed copolymer particles, the thermodynamic equations and the parameters and constants proposed in this study are applicable with reasonable accuracy to the prediction of the monomer concentration in SAN copolymer particles.

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