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Partial Swelling of Latex Particles by Two Monomers

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ABSTRACT: The swelling of polymeric latex particles with solvent and monomer is of great importance for the emulsion polymerization process in regard to composition drift and rate of polymerization. For the monomer combination, methyl acrylate-vinyl acetate, both saturation and partial swelling were determined experimentally. Theories for saturation swelling and partial swelling of the separate monomers are in good agreement with experimental results. Based on previous work an extended thermodynamic model for monomer partitioning at partial swelling of latex particles by two monomers with limited water solubility is developed. Results predicted by this model are in good agreement with observed monomer partitioning.

Introduction

Partitioning of two monomers between latex particles, monomer droplets, and the aqueous phase in an emulsion polymerization is, amongst other things, very important for modeling both the composition drift occurring during reaction and the rate of polymerization. In order to accurately describe emulsion copolymerization in terms of composition drift, monomer partitioning between the different phases should be taken into account.

Morton et al.¹ dealt with saturation swelling of latex particles primarily by monomers. On the basis of this work, Maxwell et al.^{2,3} developed a simplified thermodynamic model that deals with saturation swelling of a polymer latex by two monomers. Partial swelling of latex particles, occurring in the so-called interval III of emulsion polymerization, is also very important. During interval III there are no monomer droplets present in the system and the monomer is solubilized in both the particle and the aqueous phases. On the basis of work done by Vanzo et al.⁴ and Gardon,⁵ a simple model was developed by Maxwell et al.⁶ for the estimation of monomer partitioning where the monomer has a limited water solubility in the aqueous phase. Both models, describing saturation swelling and partial swelling, are tested for the monomer combination methyl acrylate-vinyl acetate.

On the basis of the work of Maxwell et al.^{2,3,6} an extended model is developed in this paper to predict the partial swelling of latex particles with two monomers with limited water solubilities. The results predicted by this extended model are compared with observed monomer partitioning results for the monomer combination methyl acrylate-vinyl acetate (MA-VAc). Note that the theoretical developments described in this paper are specifically for the swelling of latex particles with monomers. However, the considerations made are quite general and are valid for all partially water-soluble solvents. Furthermore, the theory can be trivially extended to take into account three or more solvents or monomers.

Theory

Morton et al.¹ considered the saturation swelling of latex particles by a monomer having limited solubility in the water phase. When the homogeneously swollen latex

particle phase is in equilibrium with the free-monomer phase, the partial molar free energy of the monomer is given by

$$\Delta F = \Delta F_m + \Delta F_s = 0 \quad (1)$$

where ΔF is the partial molar free energy of monomer, ΔF_m the contribution from the energy of mixing of monomer and polymer, and ΔF_s the contribution from the latex particle-water surface interfacial energy.

Morton et al.¹ expressed the partial molar free energy of mixing of one monomer and polymer in terms of the Flory-Huggins theory⁷

$$\Delta F_m/RT = \ln(1 - \nu_p) + \nu_p(1 - 1/\bar{M}_n) + \chi\nu_p^2 \quad (2)$$

where ν_p is the volume fraction of polymer in the latex particles, \bar{M}_n the number-average degree of polymerization, R the gas constant, T the temperature, and χ the Flory-Huggins interaction parameter. Note that, since \bar{M}_n is normally large, eq 2 may usually be written in a simpler form

$$\Delta F_m/RT = \ln(1 - \nu_p) + \nu_p + \chi\nu_p^2 \quad (3)$$

For simplicity, in the following theoretical development we use the form of eq 3 and not eq 2 (i.e., we assume $1/\bar{M}_n$ is small for the polymers of interest).

The partial molar free energy of mixing of monomer i with polymer (ΔF_{mi}) in the presence of a second monomer j is given by an equation analogous to eq 2⁷⁻⁹

$$\Delta F_{mi}/RT = \ln \nu_{pi} + (1 - m_{ij})\nu_{pj} + \nu_p + \chi_{ij}\nu_{pj}^2 + \chi_{ip}\nu_p^2 + \nu_{pj}\nu_p(\chi_{ij} + \chi_{ip} - \chi_{jp}m_{ij}) \quad (4)$$

where ν_{pi} and ν_{pj} are the respective volume fractions of monomers i and j in the latex particles, χ_{ij} is the interaction parameter between monomers i and j , and χ_{ip} and χ_{jp} are the interaction parameters between each of the respective monomers i and j and the polymer. The term m_{ij} is the ratio of the molar volumes of monomers i and j (i.e., $m_{ij} = V_{mi}/V_{mj}$, where V_{mi} and V_{mj} are the molar volumes of monomers i and j , respectively). The derivation of eq 4 involves the reasonable assumption⁸ that m_{ip} and m_{jp} , the ratios of the respective molar volumes of monomers i and j and the molar volume of polymer, are negligible compared to all other terms.

For monomer i the contribution to the interfacial free energy of a latex particle (ΔF_{si}) is given in terms of the

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Gibbs–Thomson equation^{1,8}

$$\Delta F_{si} = 2V_{mi}\gamma\nu_p^{1/3}/R_0 \quad (5)$$

where γ is the particle–water interfacial tension and R_0 the unswollen radius of the latex particle.

The partial molar free energy of monomer i in the particle phase (ΔF_{pi}) is given by the sum of the contributions from both the mixing of monomer i and polymer and the interfacial free energy.

$$\Delta F_{pi} = \Delta F_{mi} + \Delta F_{si} \quad (6)$$

The partial molar free energy of the monomer in the droplets (ΔF_{di}) can also be calculated from the Flory–Huggins lattice theory:⁷

$$\Delta F_{di}/RT = \ln \nu_{di,sat}(r) + (1 - m_{ij})\nu_{dj,sat}(r) + \chi_{ij}\nu_{dj,sat}^2(r) \quad (7)$$

The use of Flory–Huggins theory in this case will be discussed later in this paper. In the above equation $\nu_{di,sat}(r)$ represents the volume fraction of monomer i in the droplets at a certain mole ratio of the two monomers, r , and $\nu_{dj,sat}(r)$ represents the volume fraction of monomer j in the droplets at the same ratio. In this paper the postscript (r) always represents the saturation value of the quantity at a certain monomer mole ratio in the particle or droplet phases, and the subscripts a, p, and d represent respectively the aqueous phase, the polymer particle phase, and the monomer droplet phase. Note that we are always dealing with saturation swelling if there are monomer droplets present. The use of eq 7 assumes that the lattice model is valid for mixtures of small molecules; this is valid for two organic monomers of equal or similar molar volumes. Note also that due to the normally large size of monomer droplets we have not considered contributions from the monomer droplet–water interfacial free energy in eq 7 (this assumption may not be valid for a system containing very small monomer droplets).

The partial molar free energy of the monomer in the aqueous phase (ΔF_{ai}) is given by^{2,4,5,8}

$$\Delta F_{ai} = RT \ln a_i \quad (8)$$

where the activity of monomer i , a_i , is given by $a_i = (\gamma[M_i]_a)/(\gamma^\circ[M_i]_a^\circ)$, where γ is the activity coefficient of the monomer, γ° the activity coefficient of the monomer at some standard state, $[M_i]_a$ the concentration of monomer in water, and $[M_i]_a^\circ$ the concentration of monomer in water at standard state. We chose the standard state to be just homosaturation of the monomer in water; i.e., $[M_i]_a^\circ = [M_i]_{a,sat}(h)$. In this paper the postscript (h) always represents the saturation concentration in the absence of other monomers (homosaturation). The activity coefficients describe the solute–solute and the solute–solvent interactions; up to a few molar concentrations of a solute the solute–solute interactions are insignificant; hence, $\gamma = \gamma^\circ$. Therefore, eq 8 becomes

$$\Delta F_{ai} = RT \ln \left(\frac{[M_i]_a}{[M_i]_{a,sat}(h)} \right) \quad (9)$$

Equation 9 has been shown to be true for a variety of monomer–latex systems.^{2,6}

At equilibrium the partial molar free energy of each monomer will be equal in each of the three phases, i.e., the polymer particle, the monomer droplet, and the aqueous phases.

$$\Delta F_{pi} = \Delta F_{di} = \Delta F_{ai} \quad (10)$$

Applying this condition, from eqs 4–10 for saturation swelling the following equations for monomer i are

found:^{2,3,7–9}

$$\begin{aligned} \ln \nu_{pi,sat}(r) + (1 - m_{ij})\nu_{pj,sat}(r) + \nu_{p,sat}(r) + \chi_{ij}\nu_{pj,sat}^2(r) + \\ \chi_{ip}\nu_{p,sat}^2(r) + \nu_{pj,sat}(r)\nu_{p,sat}(r)(\chi_{ij} + \chi_{ip} - \chi_{jp}m_{ij}) + \\ \frac{2V_{mi}\gamma\nu_{p,sat}^{1/3}(r)}{R_0RT} = \ln \nu_{di,sat}(r) + (1 - m_{ij})\nu_{dj,sat}(r) + \\ \chi_{ij}\nu_{dj,sat}^2(r) = \ln \left(\frac{[M_i]_{a,sat}(r)}{[M_i]_{a,sat}(h)} \right) \quad (11a) \end{aligned}$$

Similarly, for monomer j we find (note in ref 2 χ_{ji} was inadvertently replaced by χ_{ij} in eq 11b. This error was corrected in ref 3.)

$$\begin{aligned} \ln \nu_{pj,sat}(r) + (1 - m_{ji})\nu_{pi,sat}(r) + \nu_{p,sat}(r) + \chi_{ji}\nu_{pi,sat}^2(r) + \\ \chi_{jp}\nu_{p,sat}^2(r) + \nu_{pi,sat}(r)\nu_{p,sat}(r)(\chi_{ji} + \chi_{jp} - \chi_{ip}m_{ji}) + \\ \frac{2V_{mj}\gamma\nu_{p,sat}^{1/3}(r)}{R_0RT} = \ln \nu_{dj,sat}(r) + (1 - m_{ji})\nu_{di,sat}(r) + \\ \chi_{ji}\nu_{di,sat}^2(r) = \ln \left(\frac{[M_j]_{a,sat}(r)}{[M_j]_{a,sat}(h)} \right) \quad (11b) \end{aligned}$$

where χ_{ji} is related to χ_{ij} by $\chi_{ji} = \chi_{ij}m_{ji}$. All other terms are as previously described, and the subscript “sat” combined with the term (r) indicates saturation values at a particular monomer ratio, r .

At partial swelling (i.e., no droplet phase) the equations will be more simple because the expression for the droplet phase can be neglected. For monomer i the equation will be

$$\begin{aligned} \ln \nu_{pi} + (1 - m_{ij})\nu_{pj} + \nu_p + \chi_{ij}\nu_{pj}^2 + \chi_{ip}\nu_p^2 + \nu_{pj}\nu_p(\chi_{ij} + \\ \chi_{ip} - \chi_{jp}m_{ij}) + \frac{2V_{mi}\gamma\nu_p^{1/3}}{R_0RT} = \ln \left(\frac{[M_i]_a}{[M_i]_{a,sat}(h)} \right) \quad (11c) \end{aligned}$$

Similarly, for monomer j

$$\begin{aligned} \ln \nu_{pj} + (1 - m_{ji})\nu_{pi} + \nu_p + \chi_{ji}\nu_{pi}^2 + \chi_{jp}\nu_p^2 + \nu_{pi}\nu_p(\chi_{ji} + \\ \chi_{jp} - \chi_{ip}m_{ji}) + \frac{2V_{mj}\gamma\nu_p^{1/3}}{R_0RT} = \ln \left(\frac{[M_j]_a}{[M_j]_{a,sat}(h)} \right) \quad (11d) \end{aligned}$$

Equation 11a–d can be used to predict monomer partitioning for latex systems containing two monomers in both saturation (eq 11a,b) and partial (eq 11c,d) swelling. There are, however, difficulties in determining the values for the interaction parameters and the interfacial tension because, amongst other things, both may be dependent upon the volume fraction of polymer in the latex particles as well as on the monomer ratio.⁷

In a manner similar to Maxwell et al.² the following assumptions for saturation swelling and for partial swelling can be made:

Assumption 1: The difference between the molar volumes of many pairs of monomers is slight; therefore, the ratio of the molar volumes of monomer i and j is well approximated by unit; i.e., $m_{ij} = m_{ji} = 1$. Note that in this case the interaction parameters χ_{ij} and χ_{ji} will be equal. Note also that this assumption validates the use of eq 7 in what follows since mole fraction is then equivalent to volume fraction. The mixing of two small molecules should, in principle, be considered in terms of mole fraction. We adopt the form of eq 7 for simplicity and note here that, because of assumption 1, further theoretical development utilizing this simplification is validated.

Assumption 2: The interaction parameters for each monomer with the same polymer are equal ($\chi_{ip} = \chi_{jp}$).

At saturation swelling these assumptions lead to the following result for monomer i :²

$$\ln \nu_{pi,sat} + \nu_{p,sat}(r) + \chi_{ij}\nu_{pj,sat}^2(r) + \chi_{ip}\nu_{p,sat}^2(r) + \nu_{pj,sat}(r) \nu_{p,sat}(r) \chi_{ij} + \frac{2V_{mi}\gamma\nu_{p,sat}^{1/3}(r)}{R_0RT} = \ln \nu_{di,sat}(r) + \chi_{ij}\nu_{dj,sat}^2(r) = \ln \left(\frac{[M_i]_{a,sat}(r)}{[M_i]_{a,sat}(h)} \right) \quad (12a)$$

An analogous equation can be derived in a similar manner for monomer j at saturation swelling.

Similarly for partial swelling we find for monomer i

$$\ln \nu_{pi} + \nu_p + \chi_{ij}\nu_{pj}^2 + \chi_{ip}\nu_p^2 + \nu_{pj}\nu_p\chi_{ij} + \frac{2V_{mi}\gamma\nu_p^{1/3}}{R_0RT} = \ln \left(\frac{[M_i]_a}{[M_i]_{a,sat}(h)} \right) \quad (12b)$$

An analogous equation can be derived for monomer j at partial swelling.

Using eq 12a for monomer i together with a similar equation for monomer j , we find for saturation swelling²

$$\ln \left(\frac{\nu_{pi,sat}(r)}{\nu_{pj,sat}(r)} \right) + \chi_{ij}(\nu_{pj,sat}(r) - \nu_{pi,sat}(r)) = \ln \left(\frac{\nu_{di,sat}(r)}{\nu_{dj,sat}(r)} \right) + \chi_{ij}(\nu_{di,sat}(r) - \nu_{dj,sat}(r)) = \ln \left(\frac{[M_i]_{a,sat}(r)}{[M_i]_{a,sat}(h)} \right) \left(\frac{[M_j]_{a,sat}(r)}{[M_j]_{a,sat}(h)} \right) \quad (13a)$$

and for partial swelling

$$\ln \left(\frac{\nu_{pi}}{\nu_{pj}} \right) + \chi_{ij}(\nu_{pj} - \nu_{pi}) = \ln \left(\frac{[M_i]_a}{[M_i]_{a,sat}(h)} \right) \left(\frac{[M_j]_a}{[M_j]_{a,sat}(h)} \right) \quad (13b)$$

Saturation Swelling of Latex Particles by Two Monomers

For saturation swelling Maxwell et al.² made one more assumption (assumption 3) which states that the term in eq 13a containing the interaction parameter for the mixing of two monomers, χ_{ij} , is rather small relative to all other terms in eq 4. The right-hand equality of eq 13a together with assumption 3 leads to the following results:²

$$\nu_{di,sat}(r) = \frac{[M_i]_{a,sat}(r)}{[M_i]_{a,sat}(h)} \quad (14a)$$

$$\nu_{dj,sat}(r) = \frac{[M_j]_{a,sat}(r)}{[M_j]_{a,sat}(h)} \quad (14b)$$

where $[M_i]_{a,sat}(r)$ and $[M_j]_{a,sat}(r)$ are the saturation solubility values for monomers i and j in the aqueous phase at a certain monomer ratio, r . Assumption 3 can only be made if either or both the values for ν_p and χ_{ij} are relatively small.

Using eq 13a with assumption 3 gives relationships between monomer concentrations in the droplet phase and the particle phase:²

$$f_{pi,sat} = f_{di,sat} \quad (15a)$$

$$f_{pj,sat} = f_{dj,sat} \quad (15b)$$

where $f_{pi,sat}$, $f_{di,sat}$, $f_{pj,sat}$, and $f_{dj,sat}$ represent respectively the monomer mole fraction of monomers i and j in the droplet and particle phases at saturation swelling. Note that in the particle phase the monomer mole fraction does not include the mole fraction of polymer. The two equations (e.g., eqs 15a,b) were shown to be approximately valid over a wide range of conditions typical for emulsion polymer systems even when the three assumptions (1-3) utilized in their derivation do not exactly hold. In a sensitivity analysis, numerical solution³ of the full equations represented by eq 11a-d showed that, given reasonable values of all interaction parameters and molar volumes of the monomers, the results represented by eq 15a,b are almost always correct. The three assumptions are of algebraic necessity only. This is a tremendously important result, since it points to the general applicability of eq 15a,b even when one or more of the assumptions described above do not hold exactly.

Polymer Phase. With the result given in eqs 15a,b, the relationship $f_{pi,sat} = [M_i]_{p,sat}(r)/([M_i]_{p,sat}(r) + [M_j]_{p,sat}(r))$ and the assumptions that (1) the total monomer concentration in the latex particles is just equal to the sum of the concentrations of the individual monomers and (2) the total monomer concentration in the latex particles is a linear function of the fraction of the monomers in the droplet phase, Maxwell et al.² developed an empirical description for the concentration of two monomers at saturation swelling within polymer latices. For a particular seed latex the concentration of monomer i within the particles at a certain monomer ratio r ($[M_i]_{p,sat}(r)$) as a function of the fraction of monomer i in the droplets is given by²

$$[M_i]_{p,sat}(r) = f_{di,sat}([M_i]_{p,sat}(h) - [M_j]_{p,sat}(h))f_{di,sat} + [M_j]_{p,sat}(h) \quad (16a)$$

Similarly, for the monomer j

$$[M_j]_{p,sat}(r) = f_{dj,sat}([M_j]_{p,sat}(h) - [M_i]_{p,sat}(h))f_{dj,sat} + [M_i]_{p,sat}(h) \quad (16b)$$

where $[M_i]_{p,sat}(h)$ and $[M_j]_{p,sat}(h)$ are the maximum saturation concentrations of monomers i and j in the latex particles at monomer homosaturation swelling. Note that the monomer mole fraction in the droplets just equals the monomer mole fraction in the polymer particles; hence, in eq 16a,b the monomer mole fractions can be replaced by $f_{pi,sat}$ and $f_{pj,sat}$ if required.

Aqueous Phase. Utilizing the three assumptions described above, Maxwell et al.² found from eq 12a and its analogue for monomer j the following relationships:

$$[M_i]_{a,sat}(r) = [M_i]_{a,sat}(h) f_{pi,sat} \quad (17a)$$

$$[M_j]_{a,sat}(r) = [M_j]_{a,sat}(h) f_{pj,sat} = [M_j]_{a,sat}(h) (1 - f_{pi,sat}) \quad (17b)$$

On the basis of eq 17a,b, the following simple relationship between the monomer mole fraction of monomer i in the polymer phase ($f_{pi,sat}$) and in the aqueous phase ($f_{ai,sat}$) can be developed:

$$f_{ai,sat} = \frac{[M_i]_{a,sat}(r)}{[M_i]_{a,sat}(r) + [M_j]_{a,sat}(r)} = \frac{f_{pi,sat}}{f_{pi,sat} \left(1 - \frac{[M_j]_{a,sat}(h)}{[M_i]_{a,sat}(h)} \right) + \frac{[M_j]_{a,sat}(h)}{[M_i]_{a,sat}(h)}} \quad (18)$$

An analogous equation for monomer j can also be developed, where the subscripts i and j in eq 18 are replaced

by j and i , respectively. Note that when $[M_i]_{a,\text{sat}}(h) \approx [M_j]_{a,\text{sat}}(h)$, the mole fraction of monomer i in the two phases, i.e., the aqueous phase and polymer phase, is equal, i.e., $f_{ai,\text{sat}} \approx f_{pi,\text{sat}}$. Note also that when monomer j has a low water solubility, i.e., $[M_j]_{a,\text{sat}}(h) \approx 0$, the monomer mole fraction of monomer i in the aqueous phase will be close to unity ($f_{ai,\text{sat}} \approx 1$).

Partial Swelling of Latex Particles by One Monomer

On the basis of the Vanzo equation, Maxwell et al.⁶ derived a semiempirical equation where the value of the sum of the residual free energy and the particle-water interfacial free-energy terms in the Vanzo equation are estimated from the saturation swelling volume fraction of polymer. The partial swelling of latex particles by one monomer is described by

$$\ln(1 - \nu_p) + \nu_p + \text{corr} = \ln\left(\frac{[M]_a}{[M]_{a,\text{sat}}(h)}\right) \quad (19)$$

where $[M]_a$ and $[M]_{a,\text{sat}}(h)$ are the respective concentrations of monomer in the aqueous phase below saturation and at homosaturation swelling. The correction term accounts for the nonconfigurational entropy (In refs 2 and 6 the term configurational entropy was inadvertently replaced by conformational entropy. This entropy term is also known as combinatorial entropy.) and enthalpy terms which, at partial swelling, were found experimentally to be relatively small and constant compared to the configurational entropy terms.^{6,7} The correction term is calculated from the Morton equation and saturation swelling data⁶

$$\text{corr} = -[\ln(1 - \nu_{p,\text{sat}}) + \nu_{p,\text{sat}}] \quad (20)$$

where $\nu_{p,\text{sat}}$ is the volume fraction of polymer in the latex particles at saturation swelling by monomer.

Partial Swelling of Latex Particles by Two Monomers

At partial swelling there is no droplet phase present so eq 13b must be used. If the polymer fraction within the particles, ν_p , is relatively large, then $\nu_{pj} - \nu_{pi}$ is small. In this case the following inequality holds: $\text{abs}(\chi_{ij}(\nu_{pj} - \nu_{pi})) \ll \text{abs}(\ln(\nu_{pi}/\nu_{pj}))$ in which abs means that the absolute values of these quantities should be used. Alternatively, if $\chi_{ij} < 1$, then this inequality also holds. The assumptions used to make this inequality will be discussed in more detail in the Results and Discussion section in light of experimental results.

Using this inequality, the simplified eq 13b becomes

$$\frac{\nu_{pi}}{\nu_{pj}} = \frac{[M_i]_a [M_j]_{a,\text{sat}}(h)}{[M_j]_a [M_i]_{a,\text{sat}}(h)} \quad (21)$$

Note that for a certain ratio of monomers, r , at saturation $[M_i]_a = [M_i]_{a,\text{sat}}(r)$ where $[M_i]_{a,\text{sat}}(r)$ is the saturation value at that ratio of monomers. Hence, the saturation values in eq 21 must be the saturation values for monomer homosaturation swelling ($[M_i]_{a,\text{sat}}(h)$ and $[M_j]_{a,\text{sat}}(h)$). This is an important result since the monomer homosaturation values are readily accessible parameters.

From saturation swelling we know that the volume fractions of monomer i over monomer j in the droplet phase are equal to the volume fractions of monomer i over monomer j in the polymer particles. Knowing this and combining eqs 14a,b and 21 gives the following equation:

$$\frac{[M_i]_a}{[M_i]_{a,\text{sat}}(r)} = \frac{[M_j]_a}{[M_j]_{a,\text{sat}}(r)} \quad (22)$$

From eqs 14a,b, 21, and 22 we also find

$$\frac{[M_i]_p}{[M_i]_{p,\text{sat}}(r)} = \frac{[M_j]_p}{[M_j]_{p,\text{sat}}(r)} \quad (23)$$

The use of eqs 22 and 23 is very convenient when realizing that with known mole fractions of monomer i within the particle phase, f_{pi} , the saturation concentrations at any monomer ratio r can be calculated directly from the saturation swelling equations (eqs 16a,b and 17a,b). Hence, eqs 22 and 23 give readily accessible relationships between the monomer concentrations of monomer i and monomer j in the aqueous phase (eq 22) and the polymer phase (eq 23) at partial swelling of the latex particles.

The monomer concentrations in the particle phase and the aqueous phase at partial swelling can be related in a manner similar to that used by Maxwell et al.⁶ when developing the semiempirical equation for the one-monomer situation (eq 19). The sum of all terms containing interaction parameters and monomer molar volumes is assumed to be approximately constant at all volume fractions of polymer. This assumption arises from the fact that the dominant term for partial swelling of latex particles is the configurational entropy of mixing. All other nonconfigurational entropy and enthalpy free energy terms have been shown to be small and approximately constant at partial swelling.⁶ For two-monomer swelling, from eq 11c for monomer i we find an equation similar to eq 19:

$$\ln \nu_{pi} + \nu_p + \text{corr}_i(r) = \ln \frac{[M_i]_a}{[M_i]_{a,\text{sat}}(h)} \quad (24)$$

where the correction term, $\text{corr}_i(r)$, for monomer i at a certain monomer mole ratio, r , accounts not only for nonconfigurational entropy and enthalpy terms but also for the different maximum concentration of monomer i in the aqueous phase at monomer ratio r compared to homosaturation swelling. The correction term is calculated from eq 11c and saturation swelling data for monomer i at a certain monomer ratio, r .

$$\text{corr}_i(r) = -(\ln \nu_{pi,\text{sat}}(r) + \nu_{p,\text{sat}}(r)) + \ln \frac{[M_i]_{a,\text{sat}}(r)}{[M_i]_{a,\text{sat}}(h)} \quad (25)$$

Note that the saturation volume fractions can be calculated from eq 16a,b and molar volumes and require only a knowledge of the homosaturation concentrations of the monomers in the particles (i.e., each monomer in the absence of the other). For monomer j analogous relationships can be derived where the subscripts i in eqs 24 and 25 are replaced by the subscript j .

Rewriting eq 21 gives a similar relationship between the polymer and aqueous phases at partial swelling to that developed for saturation swelling of latex particles (i.e., eq 18).

$$f_{ai} = \frac{[M_i]_a(r)}{[M_i]_a(r) + [M_j]_a(r)} = \frac{f_{pi}}{f_{pi} \left(1 - \frac{[M_j]_{a,\text{sat}}(h)}{[M_i]_{a,\text{sat}}(h)}\right) + \frac{[M_j]_{a,\text{sat}}(h)}{[M_i]_{a,\text{sat}}(h)}} \quad (26)$$

From this we can conclude that eq 18 holds for both saturation and partial swelling of latex particles by two monomers with limited water solubility.

The important equations for partial swelling are eqs 21 and 26, because they relate the concentration of one monomer in the aqueous phase with the concentration of the same monomer in the polymer phase, and eqs 22 and 23, because they give relationships for the concentrations

Table I. Seed Latex Recipe

ingredient	mass (g)	ingredient	mass (g)
MA	80	sodium persulfate	0.256
VAc	80	SDS	1.317
water	800	sodium carbonate	0.141

of monomer i and j in the aqueous phase (eq 22) and the polymer phase (eq 23), respectively.

Experimental Section

Materials. The seed latex used in the monomer partitioning experiments was prepared with the following materials: reagent-grade methyl acrylate (MA, Janssen Chimica, Tilburg, The Netherlands) and vinyl acetate (VAc, Janssen Chimica, Tilburg, The Netherlands), doubly distilled water, sodium persulfate (p.a., Fluka AG, Buchs, Switzerland) as initiator, sodium dodecyl sulfate (SDS, Fluka AG, Buchs, Switzerland) as surfactant, and sodium carbonate (p.a., Merck, Darmstadt, FRG) as buffer. Before use, the monomers were distilled under reduced pressure in order to remove inhibitor. The middle fraction was cut and stored at 4 °C. The monomers used in the monomer partitioning experiments were applied as received without any further purification to prevent polymerization during monomer partitioning experiments.

Seed Latex Preparation. The seed latex was prepared in a 1.3-L stainless steel reactor fitted with four baffles of 90° intervals and with a six-bladed turbine impeller. The recipe for the seed preparation is given in Table I. Reaction took place under 1.3 bar of nitrogen at 50 °C for 8 h, and thereafter the temperature was increased to 80 °C for 15 h in order to reach high conversion and to dissociate the remainder of the initiator.

Before using the poly(methyl acrylate-vinyl acetate) seed latex for monomer partitioning experiments, the latex was dialyzed in a membrane tube in order to remove excess surfactant, initiator, buffer, and monomer. The water was changed every 2 h until the conductivity of the water stayed constant in time. After this the solids content was determined by gravimetry (solids content = 16.5 wt %), the mole fraction of monomer unit MA in the polymer (f_{MA}) was determined by NMR ($f_{MA} = 0.50$), and the weight-average particle diameter was determined using dynamic light scattering (particle diameter $d_w = 90$ nm).

Monomer Partitioning. Monomer partitioning experiments were performed for the monomer system MA-VAc using the ultracentrifuge method.^{2,6} A latex with known solids content was mixed with known amounts of MA and/or VAc at room temperature in the absence of initiator. Equilibrium was reached within 24 h of shaking. The different phases, two in partial swelling and three in saturation swelling, were separated using an ultracentrifuge (45 000 rpm Centrikon T-2060, 1–2 h) at room temperature. The concentrations of MA and VAc in the aqueous phase were determined by gas chromatography (GC) using 2-propanol as internal standard. Assuming that (1) the volumes of monomer and polymer are additive and (2) the copolymer density is the average of the homopolymer densities, the monomer content in the polymer particles was determined by mass balance for partial swelling. At saturation swelling a separate droplet phase prevents determination of the monomer content in the polymer particles by mass balance. Monomer concentrations in the particles were then determined by GC after dissolving the monomer-swollen polymer phase in toluene with 2-propanol as internal standard. Determination of the dry solids content of the sample gave the polymer content which was needed to make corrections for the amount of aqueous phase within the polymer phase. The monomer droplet phase was analyzed by GC in terms of monomer ratios.

Results and Discussion

The effect of particle diameter (unswollen: 30–100 nm), temperature (20–45 °C), molecular weight ($\bar{M}_n = 87$ –15 000) and copolymer composition (Sty-MA: going from pMA to p(MA-Sty) and pSty) on one-monomer partial swelling latex particles has been shown² to be negligible within experimental error. Therefore the effect of the above-mentioned features on monomer partitioning can

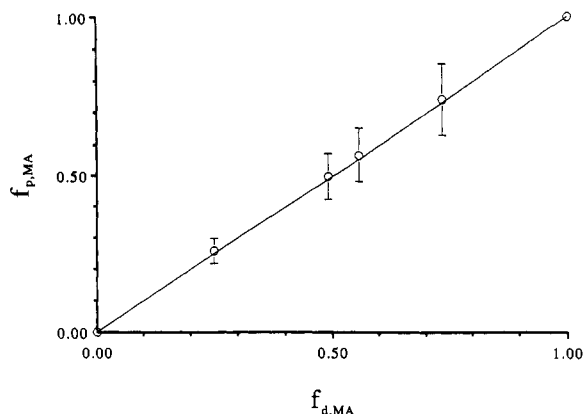


Figure 1. Comparison of theoretical predictions of eq 15a,b (—) with experimentally determined monomer fractions in latex particles ($f_{p,MA}$) as a function of the monomer fraction in the droplet phase ($f_{d,MA}$) for MA-VAc (O) in a poly(methyl acrylate-vinyl acetate) latex.

be neglected, and the use of one seed for the partitioning experiments was sufficient to develop relationships predicting monomer partitioning at partial swelling even though the particle size distribution may be broad and composition drift during seed preparation may have led to different copolymer composition.

For saturation swelling Maxwell et al.² made three assumptions to develop expressions for two-monomer partitioning. It seems reasonable to suggest that the first two of these assumptions should also be valid for partial swelling. On the basis of these three assumptions in the Theory section, relationships were derived for two-monomer partitioning at partial swelling. Considering the first two of these assumptions in regards to our experimental system, we note the following:

Assumption 1: The differences between molar volumes of monomers is generally slight. In the case of MA and VAc the differences will be extremely small because the molecular mass of MA is equal to the molecular mass of VAc and also because the densities of the monomers are nearly equal.

Assumption 2: It is hard to assess whether the interaction parameters for each monomer with the same polymer are equal ($\chi_{ip} = \chi_{jp}$) since few reliable values for these parameters exist for any monomer-polymer system. This is because it is hard to measure these parameters independently. Furthermore, the theoretical nature of these parameters is rather vague since they are supposed to include both temperature-dependent enthalpic and temperature-independent entropic terms. That the situation is even more complex has been shown by Flory,⁷ who pointed out that the interaction parameters should also be polymer concentration-dependent at high volume fractions of polymer. As has been stated by Maxwell et al.² it may be that $\chi_{ip} = \chi_{jp}$ is not exactly correct. However, it seems reasonable to suggest that the enthalpic and nonconfigurational entropic interaction of two small monomer units individually with one polymer would be of a similar nature, especially for monomers that are as alike as MA and VAc. It was noted that it was valid to make this assumption if both χ_{ip} and χ_{jp} were less than unity;³ in this case, along with assumptions 1 and 3, eq 11a,b gave the results of eq 15a,b within experimental error.

Monomer Partitioning at Saturation Swelling of Latex Particles by Two Monomers. In Figure 1 experimental data on the partitioning of MA (monomer i) and VAc (monomer j) between the particle and the monomer droplet phases are displayed. As predicted by eq 15a,b the fractions of monomer in the droplet and

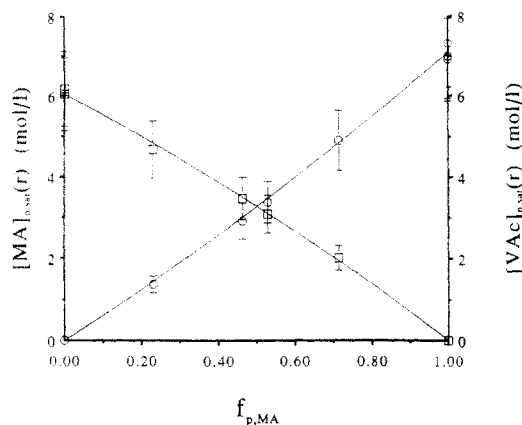


Figure 2. Comparison of the predictions of eq 16a,b (—) with experimentally determined monomer concentrations of MA (O) and VAc (□) in a poly(methyl acrylate-vinyl acetate) particle phase as a function of the monomer fractions in the polymer phase.

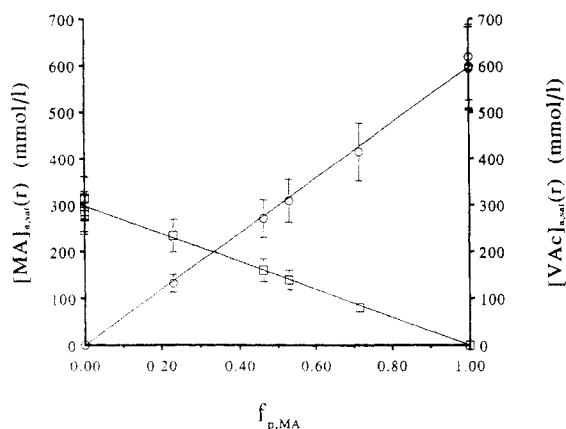


Figure 3. Comparison of the predictions of eq 17a,b (—) with experimentally determined monomer concentrations of MA (O) and VAc (□) in the aqueous phase as a function of the monomer fractions in the polymer phase.

particle phases are equal. This suggests that the three assumptions utilized by Maxwell et al.² in the derivation of this equation also are (sufficiently) valid for the monomer combination MA-VAc in a P(MA-VAc) seed latex.

That the concentrations of monomer i and j in the polymer phase and aqueous phase can be described with eqs 16a,b and 17a,b is shown by the good agreement between experiments and theory (Figures 2 and 3). Equations 16a,b and 17a,b are very useful because they only require the individual homosaturation values in the polymer and aqueous phases to be known.

Based on the relationships developed for saturation swelling and based on experiments performed, it can be concluded that the entropy of mixing of two monomers is the dominant contribution to monomer partitioning, and as a result of this the presence of polymer has no significant effect upon the ratio of the two monomers in the polymer phase. Although the monomer ratio in the polymer phase is independent of the polymer composition, the absolute monomer concentrations at saturation do depend upon the polymer and monomer type. Knowing that the polymer composition has no effect on the monomer ratios,^{2,10} we can conclude that composition drift occurring during emulsion copolymerization as a direct result of the monomer ratio within the polymer particles is independent of polymer compositions. Different polymer compositions leading to other absolute concentrations in the polymer particles will only influence the polymerization rates in the latex particles. Mass balance shows that, for monomer

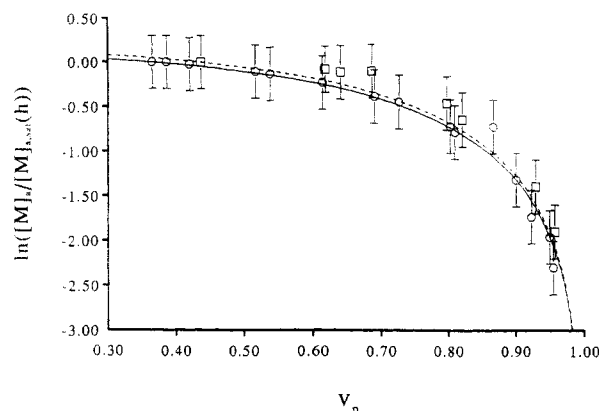


Figure 4. Comparison of the predictions of eq 19 and experimental measurements of MA (O) and VAc (□). For MA (—) the correction term used was 0.0892, and for VAc (---) the correction term used was 0.137.

systems where either one or both the monomers have a limited water solubility, changing the monomer to water ratio has an effect on the monomer ratios within the particles. In this way composition drift and polymerization rate will be changed when changing the monomer to water ratio.

Monomer Partitioning at Partial Swelling of Latex Particles by One Monomer. For monomer partitioning at partial swelling by one monomer with limited water solubility, Maxwell et al.⁶ derived a semiempirical relation where the value of the sum of the residual free energy and the particle-water interfacial free energy terms are estimated from the saturation swelling volume fraction of polymer. To use this model, only the saturation concentrations in the polymer and aqueous phases are needed. Experiments were performed to determine whether there is good agreement between this semiempirical expression and experiments. As can be seen in Figure 4, good agreement for both MA and VAc is reached when taking experimental errors into account.

The dominant factor determining monomer partitioning of one monomer at partial swelling is the free energy due to the configurational entropy of mixing of monomer and polymer.⁶ As a result of this, polymer composition has no significant effect on the monomer partitioning.

At partial swelling the relationship between the monomer concentration in the aqueous phase and the polymer phase is nonlinear leading to a monomer concentration in the aqueous phase that is closer to saturation than the monomer concentration in the polymer phase. Therefore, it can be concluded that in interval III of an emulsion polymerization with a monomer with relatively high (but still limited) water solubility, a significant amount of the monomer will be located in the aqueous phase. In this way the monomer concentration in the polymer phase will be reduced and the polymerization rate may be lowered as the monomer to water ratio is reduced (this occurs automatically during interval III of a batch emulsion polymerization). Note that other factors may effect the rate of polymerization (e.g., the Tromsdorff-Norish gel effect, initiator efficiency, diffusion-controlled propagation, etc.), but these considerations are outside the scope of this paper and are discussed elsewhere.¹¹

Monomer Partitioning at Partial Swelling of Latex Particles by Two Monomers. One relationship between the concentration of MA and VAc in the polymer particles and aqueous phases is given by eq 21. In Figure 5 experimental data are compared with the theoretical relationships developed. From Figure 5 we can conclude that there is good agreement between theory and experiments. This suggests that assumptions 1 and 2 and the

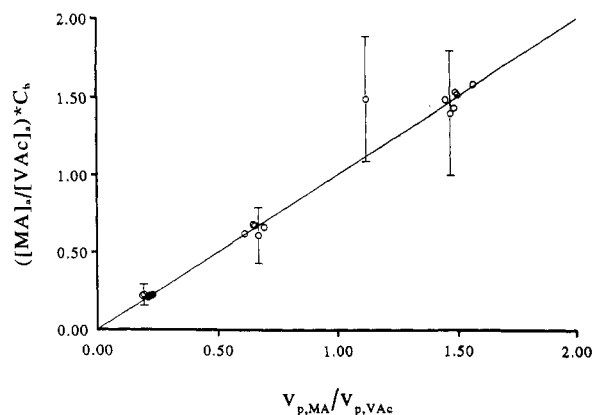


Figure 5. For MA-VAc predictions of eq 21 are compared (—) with experimentally determined monomer ratios in the aqueous phase multiplied by a constant, C_h , where $C_h = [\text{VAc}]_{a,\text{sat}}(h)/[\text{MA}]_{a,\text{sat}}(h)$ ($C_h = 0.30/0.60$ for MA-VAc) as a function of the volume fractions of monomers in the polymer phase.

inequality used during the deduction of eq 21 (assumption 3) are valid. This inequality, $\text{abs}(\chi_{ij}(\nu_{pj} - \nu_{pi})) \ll \text{abs}(\ln(\nu_{pi}/\nu_{pj}))$, only holds if ν_p is large or if $\chi_{ij} < 1$. The volume fraction of polymer can vary between the extreme values of 0 and 1. If $\nu_p = 0$ then simple calculations show that the value of $\text{abs}(\nu_{pj} - \nu_{pi})$ will be at most 50% of the value of $\text{abs}(\ln(\nu_{pi}/\nu_{pj}))$ for each monomer ratio, r (except if $\nu_{pi} = \nu_{pj}$). At $\nu_p = 0$ the value of $\text{abs}(\nu_{pj} - \nu_{pi})$ will be at most 2.5% of the value of $\text{abs}(\ln(\nu_{pi}/\nu_{pj}))$ for each monomer ratio, r . A linear relationship can give an estimated value for $\text{abs}(\nu_{pj} - \nu_{pi})$ compared to $\text{abs}(\ln(\nu_{pi}/\nu_{pj}))$ for each volume fraction of polymer in between. For typical volume fractions of polymer at partial swelling ($\nu_p = 0.6-1$) this leads to the conclusion that the maximum value of $\text{abs}(\nu_{pj} - \nu_{pi})$ compared to $\text{abs}(\ln(\nu_{pi}/\nu_{pj}))$ is $\approx 22\%$ at $\nu_p = 0.6$. Therefore, we can conclude for partial swelling that ν_p will be large enough for this inequality to be true. However, at saturation χ_{ij} still must be smaller than unity for the inequality to hold. It is important to note that a sensitivity analysis has shown,³ for typical values of all interaction parameters and molar volumes of monomers, that the three assumptions are of algebraic necessity only: numerical solutions of the full equations for two-monomer swelling described by eq 11a,d almost always verify the use of the three assumptions, and also the simplified equations that result from the use of these assumptions (e.g., eq 21).

On the basis of eq 21, relationships between monomers i and j in the aqueous phase (eq 22) and in the polymer phase (eq 23) were developed. Here also good agreement between experiments and theory was found as shown in Figures 6 and 7. From these results it can be concluded that at equilibrium at a certain monomer ratio, r , the monomer concentrations of both monomers in the aqueous phase are equally far away from saturation values at that ratio.

The concentrations of one monomer in both the polymer and aqueous phases can be related by eqs 24 and 25. As can be seen in Figure 8 experiments and theory show good agreement. Equations 24 and 25 were developed by analogy with a similar equation developed for homosaturation swelling, utilizing the concept that the free energy of mixing is dominated by configurational entropy at partial swelling. That this assumption is valid is shown by the agreement between experiments and theory in Figure 8. From eqs 24 and 25 it can be concluded that the monomer concentration in the aqueous phase is closer to saturation than the monomer concentration in the polymer phase. For monomers with relatively high (but still limited) water solubility a significant amount of the monomer will be located in the aqueous phase.

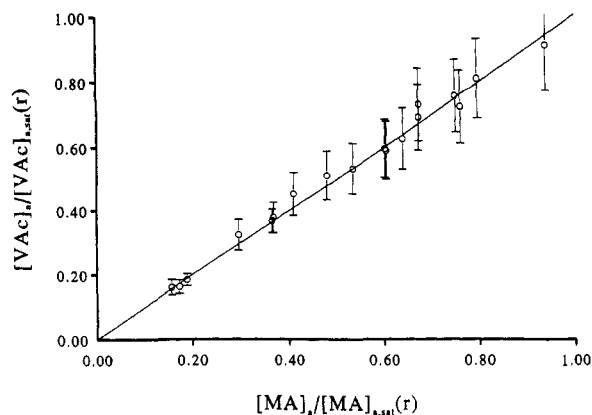


Figure 6. Comparison of the predictions of eq 22 (—) with experimentally measured concentrations for MA and VAc in the aqueous phase ($[\text{MA}]_{a,\text{sat}}(h) = 0.60$ mol/L and $[\text{VAc}]_{a,\text{sat}}(h) = 0.30$ mol/L).

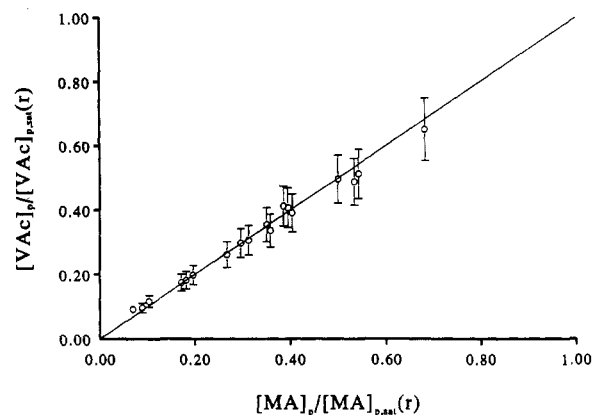


Figure 7. Comparison of the predictions of eq 23 (—) with experimentally measured concentrations for MA and VAc in the polymer particle phase ($[\text{MA}]_{p,\text{sat}}(h) = 7.05$ mol/L and $[\text{VAc}]_{p,\text{sat}}(h) = 6.11$ mol/L).

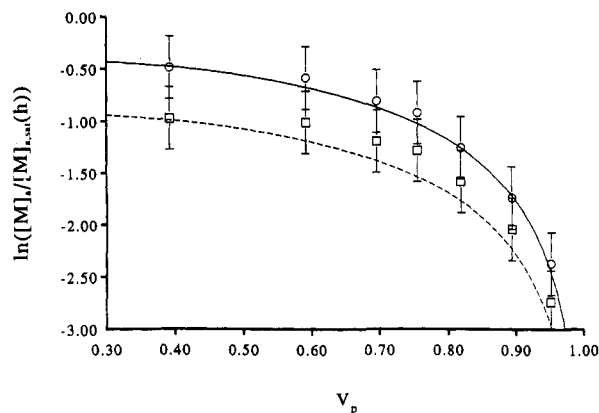


Figure 8. Comparison between predictions of eq 24 for MA (—) ($\text{corr}_{\text{MA}}(r=0.618) = 0.106$) and VAc (---) ($\text{corr}_{\text{VAc}}(r=0.382) = 0.106$) with experimental measurements for MA (○) and VAc (□). Note that the monomer mole ratio, r , is defined as the ratio of the monomer in the correction term over the other monomer.

For partial swelling, as for saturation swelling, it may be concluded that the configurational entropy of mixing of two monomers is dominant in the equilibrium reached during monomer partitioning. The monomer ratios within the polymer phase are independent of the polymer composition. However, in a manner similar to saturation swelling, absolute monomer concentrations in both the polymer and the aqueous phase do depend on the polymer composition.

The relationship between the mole fraction of monomer i in the aqueous phase and the mole fraction of monomer i in the polymer phase for saturation swelling is given by

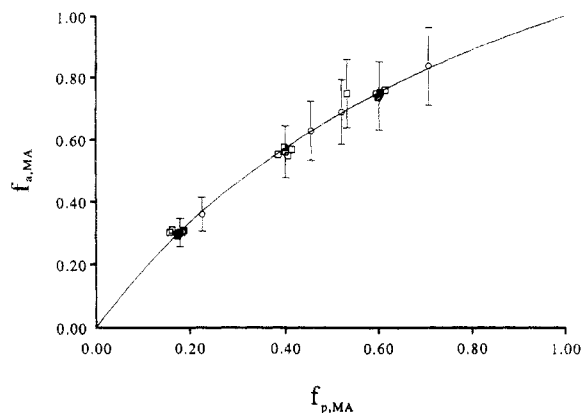


Figure 9. Comparison of the predictions of eqs 18 and 26 (—) with experimentally determined mole fractions of MA in the aqueous phase as a function of the mole fraction of MA in the polymer particle phase for MA-VAc in a poly(methyl acrylate-vinyl acetate) latex at saturation swelling (O) and at partial swelling (□).

eq 18. The exact same expression was also found for partial swelling (eq 26). Using this simple relationship(s) for both saturation and partial swelling requires only the knowledge of the individual homosaturation concentrations of the monomers in the aqueous phase. To prove that this relation indeed is valid for both partial and saturation swelling, theory and experiments are compared in Figure 9.

Conclusions

Partitioning of monomers between the different phases in an emulsion polymerization process is needed to predict the composition drift and the rate of polymerization in emulsion copolymerization reactions. For this reason relationships have been developed that predict monomer partitioning at saturation swelling by two monomers^{2,3} and monomer partitioning at partial swelling by one monomer.⁶ In this paper relationships for partial swelling by two monomers with limited water solubility have been developed to predict monomer partitioning. All relationships developed can be used if the homosaturation values of the individual monomers in both the polymer and aqueous phases are known.

Monomer partitioning at saturation swelling can be predicted with the simplified relationships developed by Maxwell et al.² This can be concluded from comparing theory with experiments performed for the monomer system MA-VAc at saturation swelling. To use these equations, only the individual homosaturation values of the monomers in the polymer particles and the aqueous phase are needed. With theory and experiments it has been shown that the mixing of two monomers is independent of the polymer type and that the ratios of monomers in the droplet and particle phases are equal. Only the absolute value of the degree of swelling depends on the monomer and polymer type. These results were based on the finding that the entropy of mixing of two monomers is the dominant contribution to the thermodynamic equilibrium reached.

Partial swelling of latex particles with one monomer can be described with the semiempirical relation developed by Maxwell et al.⁶ as has been shown by the good agreement between theory and experiments. This semiempirical

relation is based on the findings that both the interfacial tension and the residual free energy terms do not significantly influence the degree of partial swelling and that the free energy of monomer partitioning is dominated by the contribution of the configurational entropy of mixing of monomer and polymer.

For partial swelling with two monomers with limited water solubilities simple relationships have been developed to predict the monomer concentrations and fractions within the different phases. Comparing experimental results with the developed relationships showed excellent agreement. The use of these relationships merely requires the values for the individual homosaturation concentrations in the particle and aqueous phases. In a manner similar to the saturation swelling theory, the basic principle of the equations is that the entropy of mixing of two monomers at partial swelling is the dominant contribution to the equilibrium. The monomer ratio within the polymer particle is therefore independent of the polymer composition.

The good agreement between experimental data and theory for monomer partitioning at both saturation and partial swelling suggests that the theoretical development accurately describes the thermodynamics of latex particle swelling. With the relationships developed for saturation and partial swelling the mole fraction of monomer *i* and the absolute concentrations of monomers *i* and *j* within the particle phase can be determined. Using the mole fraction of monomer *i* within the particle phase enables one to predict composition drift occurring in emulsion copolymerizations, and using the absolute concentrations of monomers *i* and *j* in the particle phase can lead to a better understanding of the rates of polymerization.

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