Thermodynamics of swelling of latex particles with two monomers

Citation for published version (APA):

Maxwell, I. A., Kurja, J., van Doremale, G. H. J., & German, A. L. (1992). Thermodynamics of swelling of latex particles with two monomers. *Makromolekulare Chemie*, 193(8), 2065-2080.
<https://doi.org/10.1002/macp.1992.021930824>

DOI:

[10.1002/macp.1992.021930824](https://doi.org/10.1002/macp.1992.021930824)

Document status and date:

Published: 01/01/1992

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Thermodynamics of swelling of latex particles with two monomers

Ian A. Maxwell*, Jenci Kurja, Gerard H. J. Van Doremale^{a)}, Anton L. German

Department of Polymer Chemistry and Technology, University of Technology,
5600 MB Eindhoven, The Netherlands

(Date of receipt: October 18, 1991)

SUMMARY:

The partitioning of two monomers between the latex particle, monomer droplet and aqueous phases of an emulsion polymer latex are measured at saturation swelling of the latex particle phase (corresponding to intervals I and II of an emulsion polymerization). The monomer and polymer types are varied systematically and the experiments are performed at two temperatures. The results of these experiments correspond well to a simplified thermodynamic theory of the saturation swelling of an emulsion polymer with two monomers, in which it is realized that the fraction of one monomer is equivalent in the latex particle and monomer droplet phases. Further, it is shown that Henry's law holds for monomers, both in the absence and in the presence of swollen latex particles. A simple empirical relationship is developed whereby the concentration of two monomers at any ratio can be calculated from the individual saturation concentration of the two monomers in the latex of interest.

Introduction

The swelling of polymeric latex particles with solvents and monomers is of great importance for the emulsion polymerization process. For example, consider the rate of an emulsion polymerization: the monomer concentrations in all of the latex particle, monomer droplet and aqueous phases can be critical factors that may determine, *inter alia*, the rate of polymerization directly. The monomer concentration in the particle phase may also determine the rate of free-radical exit from latex particles¹⁾ and the initiator efficiency²⁾; these also influencing the rate of polymerization. It should also be noted that typical rates of emulsion polymerization are such that thermodynamic equilibrium of monomer between the phases during polymerization is usually achieved. The absolute concentrations and concentration ratios of monomers in the latex particles of an emulsion polymerization are also key parameters in understanding copolymer composition and the inter-molecular and intra-molecular polymer structure.

The saturation swelling of latex particles by two monomers has been dealt with by various workers^{3–5)}. In this paper a simplified thermodynamic model that deals with saturation swelling of polymer latex by two monomers is developed. This model is based on experimental monomer partitioning data, in which the monomer concentrations in the latex particle, monomer droplet and aqueous phases are measured for a range of monomer and polymer types. This paper will deal exclusively with swelling

^{a)} Current address: California Institute of Technology, Arnold and Mabel Beckman Laboratories, Pasadena, CA91125, USA.

of latex particles by two monomers, but the considerations made are quite general and should apply to most solvents. Furthermore, the approach developed in this study can be easily extended to deal with systems of 3 or more solvents and/or monomers.

Theory

Morton et al.⁶ 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.⁶ expressed the partial molar free energy of mixing of one monomer and polymer in terms of the Flory-Huggins theory⁷

$$\Delta F_m/(RT) = \ln(1 - v_p) + v_p \cdot \left(1 - \frac{1}{\bar{M}_n}\right) + \chi v_p^2 \quad (2)$$

where v_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:

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

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 polymer species 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. (2)^{3,4,7}

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

where v_{pi} and v_{pj} are the respective volume fractions of monomer i and j in the latex particles, χ_{ij} 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 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 monomer i and j , respectively). The derivation of Eq. (4) involves the reasonable assumption³ 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 as compared with 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 Gibbs-Thomson equation^{3,6)}

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

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:³⁾

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

In this term v_{di} represents the volume fraction of monomer i in the droplets, and v_{dj} the volume fraction of monomer j in the droplets. The use of Eq. (7) assumes that the lattice model is valid for mixtures of small molecules; this may be valid for two organic monomers. 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^{3,8-10)}

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

where the activity of monomer i , a_i , is well approximated by p_i/p_i^0 , the ratio of the vapor pressures of the monomer i below (p_i) and at saturation (p_i^0)^{9,10)}. It has been shown^{9,10)} that, since Henry's law holds for latex-free water, the ratio p_i/p_i^0 is well approximated by $[M_i]_a/[M_i]_{a, \text{sat}}$ the ratio of the water solubilities of monomer i below saturation ($[M_i]_a$) and at saturation in the absence of other monomers ($[M_i]_{a, \text{sat}}$). In the Results and discussion of this paper we will show that, in accord with previous results¹⁰⁾, Henry's law also holds in the presence of latex particles. Eq. (8) then becomes:

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

At equilibrium the partial molar free energy (or the chemical potential) of each monomer will be equal in each of the three phases.

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

Applying this condition, from Eqs. (4)–(10) we find the following equations for monomer i :

$$\begin{aligned} \ln v_{pi} + (1 - m_{ij})v_{pj} + v_p + \chi_{ij} \cdot v_{pj}^2 + \chi_{ip} \cdot v_p^2 + v_{pj} \cdot v_p \cdot (\chi_{ij} + \chi_{ip} - \chi_{jp} \cdot m_{ij}) \\ + \frac{2V_{mi} \cdot \gamma v_p^{1/3}}{R_0 \cdot RT} = \ln v_{di} + (1 - m_{ij})v_{dj} + \chi_{ij} \cdot v_{dj}^2 = \ln \left(\frac{[M_i]_a}{[M_j]_{a, \text{sat}}} \right) \end{aligned} \quad (11a)$$

Similarly, for monomer j we find:

$$\begin{aligned} \ln v_{pj} + (1 - m_{ji})v_{pi} + v_p + \chi_{ij} \cdot v_{pi}^2 + \chi_{jp} \cdot v_p^2 + v_{pi} \cdot v_p \cdot (\chi_{ij} + \chi_{jp} - \chi_{ip} \cdot m_{ji}) \\ + \frac{2V_{mj} \cdot \gamma v_p^{1/3}}{R_0 \cdot RT} = \ln v_{dj} + (1 - m_{ji})v_{di} + \chi_{ij} \cdot v_{di}^2 = \ln \left(\frac{[M_j]_a}{[M_i]_{a, \text{sat}}} \right) \end{aligned} \quad (11b)$$

Eq. (11 a–b) can be used to predict and/or model partitioning data for latex systems with two monomers. There are, however, some difficulties associated with the use of these equations:

(1) First, the use of Eq. (11) requires known values for the three interaction parameters. Flory⁷⁾ pointed out two complications involved with the use of interaction parameters: (a) For systems with high volume fraction of polymers (which is certainly the case for swollen latex particles) the interaction parameters cannot be independent of the volume fraction. Hence, the original Flory-Huggins equation, and its two-monomer analogue (Eq. (4)) can only be applied as useful semi-empirical relationships, where the terms containing an interaction parameter can be thought of as residual free-energy terms, containing both temperature-dependent enthalpic terms and temperature-independent entropic terms. (b) The situation where the Flory-Huggins equation is used as a semi-empirical equation can be satisfactory for systems with one monomer, since there is only one adjustable parameter (χ). However, for two monomer systems there are at least three adjustable interaction parameters. These may be determined by fitting Eq. (11) to experimental data, but often do not offer unique values for these fitted parameters. An alternative approach for estimating interaction parameters, the use of mutual solubility measurements, can be less than satisfactory³⁾.

(2) An extra difficulty for the polymer latex situation is that the value of the particle-water interfacial tension is difficult to determine experimentally. Therefore, in systems with one monomer the interfacial tension is often determined by fits to the Morton equation⁶⁾. However, it should be noted that the interfacial tension may change with the ratio of monomer i to j , and also with the total concentration of monomer at the interface, and hence also the volume fraction polymer in the latex particles.

It should be noticed, that, at saturation swelling of latex particles by two monomers, the variables of interest are the concentrations of monomer i and j in each of the three phases. The theory that describes this situation consists of four equations (Eq. (11 a–b)) and at least four unknown parameters (χ_{ij} , χ_{ip} , χ_{jp} , γ) all of which may vary with the volume fraction polymer and/or the ratio of monomers within the latex

particles, thereby introducing many more unknown variables. There are methods for estimating the values of these parameters, and hence predicting monomer concentrations in each phase. In this paper, however, we present an alternative approach: simplifications to theory of two monomer swelling of latex particles (Eq. (11 a–b)) are described in the rest of this section.

In an attempt to simplify Eq. (11) three assumptions are made:

Assumption (1): For many pairs of monomer the differences between the molar volumes of the monomers is slight. If this is the case the ratio of the molar volumes of monomer i and j is well approximated by unity, i.e. $m_{ij} = m_{ji} = 1$.

Assumption (2): The contribution to the partial molar free energy arising from the residual (enthalpic and non-conformational entropic) partial molar free energy of mixing of the two monomers is small relative to all other terms in the expressions (Eq. (7)) describing the partial molar free energy of monomers in the *droplet* phase.

The two above assumptions allow us to rewrite simpler forms for the right-hand equalities in Eq. (11):

$$v_{di} = \frac{[M_i]_a}{[M_i]_{a, \text{sat}}} \quad (12a)$$

$$v_{dj} = \frac{[M_j]_a}{[M_j]_{a, \text{sat}}} \quad (12b)$$

These equations are simply in the form of Henry's law, which has been shown to hold for partially water-soluble organic solvents in the absence of latex particles^{9,10}. In the Results and discussion of this paper we will present experimental evidence for the validity of Eq. (12) for partially soluble organic monomers in the presence of latex particles.

We now consider the relationships between the monomer concentrations in the particle phase and in the droplet phase: we seek simplifications to the left-hand equalities in Eq. (11). Ugelstad et al.³ made the following two assumptions:

Assumption (3): The interaction parameters for each monomer with the same polymer are equal ($\chi_{ip} = \chi_{jp}$). The basis for the use of this assumption will be discussed in light of experimental results in the Results and discussion.

Assumption (1) as above, namely that $m_{ij} = m_{ji} = 1$.

Ugelstad et al.³ incorrectly stated that the assumptions (3) and (1) are sufficient to show that the ratios of the volume fractions of monomer i to j are equal in both the latex particle and monomer droplet phases. In fact, the use of these two assumptions in Eq. (11 a–b) gives:

$$\ln \left(\frac{v_{pi}}{v_{pj}} \right) - \ln \left(\frac{v_{di}}{v_{dj}} \right) = \chi_{ij} \cdot [(v_{dj} - v_{di}) - (v_{pj} - v_{pi})] \quad (13)$$

Another important assumption, already made in assumption (2) for the monomer droplet-water phase situation, needs to be made to arrive at the situation where the ratios of the volume fractions of monomers i and j are equal in the particle and droplet phases:

Assumption (2) above: The contribution to the partial molar free energy arising from the residual (enthalpic and non-conformational entropic) partial molar free energy of mixing of the two monomers is small relative to all other terms in Eq. (4). This result can be arrived at by stating that either or both of the values v_p or χ_{ij} are relatively small. Note that, in the case v_p is relatively small, assumption (2) is not made. However, for Eq. (12a–b) to hold the value of χ_{ij} must still be relatively small. Using this assumption Eq. (13) reduces to:

$$\frac{v_{pi}}{v_{pj}} = \frac{v_{di}}{v_{dj}} \quad (14)$$

Eq. (14) relates the ratios of the volume fractions (or concentrations) of monomers i and j in the latex particles to those in the droplet phase. From Eq. (14) we can write the following equalities

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

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

where f_{pi} , f_{di} , f_{pj} and f_{dj} represent, respectively, the monomer volume fraction of monomers i and j in the droplet and particle phases. Note that in the particle phase these monomer fractions relate only to the volume of one monomer as a fraction of the total volume of both monomers in the particles (i.e. the volume of the polymer in the latex particles is not included in these fractions). Also note that, since we have assumed that the two monomers have equal molar volumes in the derivation of these equations (assumption (1) above), the monomer volume fractions also represent the monomer molar fractions.

We have managed to simplify Eq. (11a–b) such that the ratio of the concentrations of monomers i and j in the particle and monomer droplet phases can be equated. Given the fraction of each monomer in the droplet phase, the simplified equations also allow the calculation of the concentration of each monomer in the aqueous phase. However, the aim of this paper is also to present a method whereby the actual concentrations of two monomers in the particle phase can be calculated. It must be realized that, although the residual partial molar free energy and the free energy associated with the interface do not, in the simple theory described by Eqs. (14) and (15), influence the ratio of the concentration of the two monomers in the latex particles, they do influence the absolute values of the concentration of each monomer in the particles. This is simply because the total degree of swelling of latex particles is restricted by the surface free energy and the residual free energy. In the Results and discussion of this paper we will introduce a new method for estimating the concentration of two monomers in the latex particles, requiring only the individual saturation concentrations of the two monomers in the latex particles of interest.

Finally, we would like to note that the result that the fractions of each monomer are equal in the polymer and free-monomer phases is not restricted to the emulsion latex situation. The equations developed are quite general, and are implicitly assumed in the use of the copolymer equation with low-conversion bulk polymerization data — the

common method for finding copolymerization reactivity ratios. In these experiments it is normally assumed that the monomer mole ratios are equal in the monomer feed (or free organic phase) and at the polymerization site, where the presence of polymer must influence the absolute monomer concentrations, but not, according to the theory above, the mole fraction of the two monomers. Since all of the equations that describe the copolymerization experimental observables (i. e. copolymer composition, polymer sequence distributions and the rate of polymerization) depend only upon the ratio of the monomer concentrations, the effect of polymer upon the absolute concentrations of the individual monomers has no influence upon these experimental observables.

Experimental part

Materials

Reagent grade styrene (STY), butyl acrylate (BA) and methyl acrylate (MA) (Merck) were distilled under reduced nitrogen pressure in order to remove inhibitor. The middle fraction was cut and stored at 4 °C. The water was distilled twice, Potassium peroxodisulfate (Merck p. a.), dodecanethiol (Merck p. a.) and sodium dodecyl sulfate (SDS, Fluka) were used without further purification.

Seed latex preparation

The seed latices were prepared in a glass reactor under 1,7 atm. nitrogen pressure at 50 °C for both MA and BA and also for coolymerizations containing these two monomers, and at 70 °C for STY. The recipes are given in Tab. 1. After approximately 24 h the temperature was increased to 90 °C for 3 h in order to dissociate the remainder of the initiator. After polymerization initiator fragments, unreacted monomer and most of the free surfactant were removed by dialysis.

Tab. 1. Seed latex recipes (MA, BA and copolymerizations at 50 °C; STY at 70 °C)

Ingredient	Mass in g
MA, BA, STY (total)	30,0
Water	750,0
Potassium peroxodisulfate	0,2
Dodecanethiol	0,3
SDS	2,0

Particle sizing

Particle morphology and size were examined by means of transmission electron microscopy and dynamic light scattering. UV hardening of the soft poly(methyl acrylate) particles prevented melting under the microscope beam. All the kinds of latex particles used in this study are listed in Tab. 2.

Monomer partitioning

Monomer partitioning experiments were performed for three different pairs of monomers, STY-MA, STY-BA and MA-BA. Three polymer latices were used for the partitioning experiments for

Tab. 2. Seed latex composition and mean radius

Monomer system	Polymer composition (mole ratio)	Unswollen radius in nm
STY-MA	STY	89
	STY : MA (50 : 50)	63
	MA	50
STY-BA	STY	43
	STY : BA (25 : 75)	50
	BA	80
MA-BA	MA	65
	MA : BA (50 : 50)	84
	BA	73

each monomer pair. In each experiment a latex of known solid content and polymer composition (listed in Tab. 2) was mixed with known amounts of the two monomers in the absence of initiator. In all experiments sufficient water was added to ensure that the solid content in each experiment was ca. 5–10 wt.-% (it was found that varying latex solid content had no influence on the partitioning results). The system was allowed to reach equilibrium by shaking (for at least 24 h) while thermostated at the required temperature. The phases (swollen polymer particle, monomer droplet and aqueous phases) were separated using an ultracentrifuge (Centrikon T-2060, 55 000 RPM) thermostated to the same temperature as above. The swollen particles could not be analyzed without some residual aqueous phase. Monomer concentrations in the particles were determined by gas chromatography (GC) after dissolving the monomer-swollen polymer phase (with some aqueous phase content) in acetone with some toluene as an internal standard, or alternatively in the case of polystyrene latices, after dissolving in toluene with 2-propanol as internal standard. Determination of the dry solid content of the sample gave the polymer content. The concentration of MA in the aqueous phase was determined after adding a standard 2-propanol solution in water to a sample of the aqueous phase. For the determination of monomer content in the polymer particles appropriate corrections were made for the monomer contained in the residual aqueous phase. The monomer droplet phase was analyzed by GC in terms of the monomer ratios. In order to calculate the monomer concentrations inside the particles, the volumes of all components within the particles (monomer and polymer) were assumed to be additive. Copolymer densities were calculated by the appropriate averaging of the densities of the homopolymers. The partitioning experiments were carried out at 20 °C for STY-MA and STY-BA, and at 35 °C for MA-BA.

Saturation concentration of MA in aqueous phase

The effect of surfactant concentration upon the saturation coconcentration of MA in the aqueous phase at various temperatures was investigated. MA was mixed with water containing various concentrations of surfactant (SDS). GC analysis of the aqueous phase was carried out as above. It was found (Fig. 1) that the saturation concentration of MA in the aqueous phase was virtually independent of the SDS concentration. Further, the concentration of MA in water increased with decreasing temperature. This was subscribed to stronger hydrogen bonding at lower temperatures. From these results we can be sure that the determination of concentrations of MA in the aqueous phase was free of artifactual effects arising from varying surfactant concentrations in the aqueous phase. All partitioning experiments were carried out with less than 0,5 g/L free SDS in the aqueous phase: this value being well below the critical micelle concentration of SDS at the experimental temperatures.

Fig. 1. Experimentally determined saturation concentrations of MA in water as a function of SDS concentration at 4 °C (full squares), 20 °C (empty squares), 35 °C (full circles) and 45 °C (empty circles)

Results and discussion

Monomer partitioning between the latex particle phase and monomer droplet phase

Monomer fractions in the latex particle phase and monomer droplet phase

In Fig. 2 experimental data on the partitioning of methyl acrylate (MA), styrene (STY) and butyl acrylate (BA) between the particle and monomer droplet phases for a variety of seed latices are displayed. The seed latices used were the two homopolymers of the respective monomers and a copolymer of the two monomers. It is apparent that in every case the fraction of the monomer in the droplet and particle phases are equal, independent of the polymer type, the temperature and the monomer type. This is exactly the result predicted by Eq. (15) and suggests that the three assumptions utilized in the derivation of this equation are valid. We now consider these three assumptions:

Assumption (1): The first assumption is that the molar volumes of the monomer are equal. The molar volume of the three monomers used in this study are listed in Tab. 3. It is apparent that the ratio of the molar volumes of the monomers do not deviate far from unity. Hence assumption (1) appears valid for the systems under investigation.

Assumption (2): For the latex particle-monomer droplet case this assumption states that either or both of the values of v_p or χ_{ij} are small, and hence in Eq. (13) the following inequality holds, $\chi_{ij} \cdot [(v_{pi} - v_{pj}) - (v_{dj} - v_{di})] \ll \ln(v_{pi}/v_{pj})$ and $\ll \ln(v_{di}/v_{dj})$. Experimental evidence for this assumption is given in Fig. 2. In the following section the actual monomer concentrations within the latex particles of all three monomers utilized in this study are considered. Typically, the volume fraction of polymer within the particle at saturation swelling ranges from $v_p = 0.1$ to 0.4 . Hence, the term in Eq. (13), $\chi_{ij} \cdot [(v_{pj} - v_{pi}) - (v_{dj} - v_{di})]$, is relatively small, because of the relatively small values of the volume fraction of polymer and also because of the small values of χ_{ij} (which will be demonstrated below).

Assumption (3): It is hard to assess whether the value of the interaction parameters of monomers i and j with polymer would be equivalent, i.e. whether $\chi_{ip} = \chi_{jp}$, since few, if any, dependable values for these parameters exist for any monomer-polymer system. This is simply because of the difficulty of independently measuring these parameters and also the vague theoretical nature of these parameters. Interaction parameters were originally devised to describe the enthalpy of mixing of monomer and polymer, but now are considered to incorporate both temperature-dependent enthalpic

Fig. 2. Experimentally determined monomer fractions in latex particles as a function of the monomer fraction in the droplet phase and theoretical predictions of Eq. (15) (full line). (a) STY-MA at 20°C with polystyrene latex (empty squares), poly(styrene-co-methyl acrylate) latex (full squares) and poly(methyl acrylate) latex (empty circles). (b) STY-BA at 20°C with polystyrene latex (empty squares), poly(styrene-co-butyl acrylate) latex (full squares) and poly(butyl acrylate) latex (empty circles). (c) MA-BA at 35°C with poly(methyl acrylate) latex (empty squares), poly(methyl acrylate-co-butyl acrylate) latex (full squares) and poly(butyl acrylate) latex (empty circles).

and temperature-independent entropic terms. Flory⁷⁾ pointed out the original derivation of the Flory-Huggins theory for a system of one monomer resulted in an interaction parameter that should be polymer concentration-dependent at high volume fractions of polymer. The situation is obviously more complex for a system with two monomers. It may be that the assumption that $\chi_{ip} = \chi_{jp}$ is not exactly correct, but experimental evidence would suggest that this equality is approximately correct. It does not seem unreasonable to suggest that the enthalpic and non-conformational entropic interaction of two small monomer units individually with one polymer would be of a similar nature.

The validity of Eq. (14), that is the equivalence of the ratio of the volume fractions of monomers in the latex particle and droplet phases, implies that the significant

contributions to the swelling of latex particles by monomers are the partial molar free energies associated with both the conformational entropy of mixing of monomers and polymer and that associated with the interfacial tension. In the case of swelling by two monomers, both monomers are restricted in their degree of swelling by the same interfacial tension, hence this factor does not appear in Eq. (14). The presence of polymer in the latex particle does not greatly influence the mixing of the two monomers, since the entropy of mixing of two small molecules appears to dominate over all the other thermodynamics of mixing, and especially that of monomer and polymer. It is also for this reason that the residual free energy of interaction between two monomers can be neglected in both the latex and monomer droplet phases.

Monomer concentrations in the particle phase

We have already established that the volume and mole fraction of monomers in the particle and droplet phases of the systems at hand are equal to within experimental error. However, often it is the actual concentrations of the monomers in the latex particles that are of interest.

In Fig. 3 the concentrations of each monomer in the various polymer particle phases are plotted against the fraction of one monomer in the droplet phases. It is apparent that the absolute value of the degree of swelling does depend upon polymer and monomer type. In general, the more water-soluble the monomer the greater the concentration of this monomer in the particles (i. e. $[MA]_p > [BA]_p > [STY]_p$). This is probably a result of the lower latex particle-water surface tensions associated with more water-soluble monomers^{9,11}). However, as stated previously there are numerous unknown parameters in the complete model for latex particle swelling described by Eq. (11a–b): in fact too many to unambiguously determine the values of these parameters, especially when it is realized that the interfacial tension may change with the monomer ratio, and to a lesser degree so may the interaction parameters as the volume fraction of polymer changes with varying monomer ratios. In what follows we describe an empirical technique for the estimation of the concentrations of two monomers at saturation swelling within polymer latices.

In this approach we make two assumptions: (1) The result given by Eq. (15a–b), namely that the ratio of the fraction of each monomer is equal in the latex particle and droplet phases. (2) The second assumption is that the total monomer concentration in the latex particles is just equal the sum of the concentrations of the individual monomers. This total monomer concentration is assumed to be a linear function of the fraction of the monomers in the droplet phase. The impetus for this assumption arose from the experimental observation that the total monomer concentration displays relatively linear behavior as a function of the fraction of one monomer in the droplet phase (Fig. 4). In this case, all that is required to predict the concentration of two monomers in a particular latex, at any ratio of these two monomers in the feed, is the concentrations of the two monomers when they exclusively swell the particular latex. Hence, for a particular seed latex the concentration of monomer i within the particles (C_i) as a function of the fraction of monomer i in the droplets is given by:

$$C_i = f_{di} \cdot ([C_{i,m} - C_{j,m}]f_{di} + C_{j,m}) \quad (16a)$$

Similarly, for monomer j we find

$$C_j = f_{dj} \cdot ([C_{j,m} - C_{i,m}]f_{dj} + C_{i,m}) \quad (16b)$$

where $C_{i,m}$ and $C_{j,m}$ are the maximum saturation concentrations of monomers i and j in the latex particles (i.e. homo-monomer swelling concentrations of the latex).

Fig. 3. Experimentally determined monomer concentration in the latex particle phase as a function of the monomer fraction in the droplet phase with theoretical predictions of Eq. (16).

(a) STY-MA at 20°C. MA concentrations (empty symbols), STY concentrations (full symbols). Polystyrene latex (squares and full line), poly(styrene-co-methyl acrylate) latex (circles and dashed line) and poly(methyl acrylate) latex (triangles and dotted line). (b) STY-BA at 20°C. STY concentrations (empty symbols), BA concentrations (full symbols). Polystyrene latex (squares and full line), poly(styrene-co-butyl acrylate) latex (circles and dashed line) and poly(butyl acrylate) latex (triangles and dotted line). (c) MA-BA at 35°C. MA concentrations (empty symbols), BA concentrations (full symbols). Poly(methyl acrylate) latex (squares and full line), poly(methyl acrylate-co-butyl acrylate) latex (circles and dashed line) and poly(butyl acrylate) latex (triangles and dotted line)

In Fig. 3 the predictions of Eq. (16a–b) are compared to experiment. It can be seen that in all cases Eq. (16a–b) provides adequate predictions of the experimental data. Therefore, for the systems studied, if the maximum saturation concentration of each

Tab. 3. Molar volumes and ratio of molar volumes for the monomers utilized in this study

System <i>i-j</i>	Temp. in °C	$V_{m_i}/(\text{dm}^3 \cdot \text{mol}^{-1})$	$V_{m_j}/(\text{dm}^3 \cdot \text{mol}^{-1})$	m_{ij}
STY-MA	20	0,115 (STY)	0,090 (MA)	1,3
STY-BA	20	0,115 (STY)	0,140 (BA)	0,8
MA-BA	35	0,093 (MA)	0,142 (BA)	0,7

monomer in the latex particles of interest is known then the concentration of both monomers at all monomer ratios can be predicted by Eq. (16a–b).

Methyl acrylate partitioning between aqueous phase and monomer droplet phase

The concentration of MA in the aqueous phase was measured as a function of the MA concentration in the droplet phase with STY as comonomer without and with the presence of a separate swollen latex particle phase (utilizing STY-MA copolymer latex) at 20 °C (Fig. 5).

Only the concentration of MA in the aqueous phase was determined since its aqueous-phase concentration is much higher than that of styrene, allowing much greater accuracy of gas chromatographic determination of the MA concentration in the aqueous phase during mutual swelling experiments. The predictions of Eq. (12) are in excellent agreement with experiment (Fig. 5). From these results we can state that Henry's law is obeyed for MA and probably other partially water soluble monomers, both in the presence and absence of a swollen latex particle phase when there is a separate monomer droplet phase present. In the case where swollen latex particles are present both the organic phases are saturated with monomer(s), and since we have already shown that the ratio of the two monomers is equivalent for the systems in this study it is not surprising that latex particles and monomer droplets are indistinguishable in terms of how they influence the aqueous-phase monomer concentrations.

Conclusions

For the systems studied the simplified Eqs. (14) and (15) that describe the saturation partitioning of partially water soluble monomers between the latex particle and droplet phases adequately predict the fraction of each monomer in the two phases. These simplified equations state that the ratio of the two monomers, and also the fraction of each monomer, are equal in the droplet and latex particle phases. This result is based upon the following assumptions: Assumption (1): the molar volumes of the monomers are not too dissimilar, which is a reasonable assumption for most monomer pairs. Assumption (2): the contribution to the overall thermodynamic problem of the residual partial molar free energy of mixing of the two monomers within the latex particles is small compared to the contribution of the conformational entropy of mixing of the two monomers. The presence of the polymer has no significant effect upon the ratio of the two monomers since the entropy of mixing of the two monomers contributes the

Fig. 4. Experimentally determined total monomer concentrations in the latex particle phase as a function of the monomer fraction in the droplet phase. (a) STY-MA at 20 °C with polystyrene latex (empty squares), poly(styrene-co-methyl acrylate) latex (full circles) and poly(methyl acrylate) latex (empty triangles). (b) STY-BA at 20 °C with polystyrene latex (empty squares), poly(styrene-co-butyl acrylate) latex (full circles) and poly(butyl acrylate) latex (empty triangles). (c) MA-BA at 35 °C with poly(methyl acrylate) latex (empty squares), poly(methyl acrylate-co-butyl acrylate) latex (full circles) and poly(butyl acrylate) latex (empty triangles)

dominant thermodynamic effect. Assumption (3): The interaction parameters for each monomer with polymer are equal, or at least similar. This assumption seems reasonable since these interaction parameters describe the enthalpic and non-conformational entropic partial molar free energy of mixing of two small molecules with the one polymer.

The prediction of the concentration of two monomers in a single polymer latex phase is facilitated by the above result, namely that the fractions of each monomer in the particle and droplet phases are equal. Prediction of the concentration of each monomer in the latex particles requires the further experimentally observed result that the overall concentration of monomer in the latex particles is an approximate linear function of the fraction of each monomer in the particle and droplet phases. Given the values of

Fig. 5. Experimentally determined MA concentrations in the aqueous phase as a function of the fraction of MA in the droplet phase with STY as co-monomer at 20°C in the presence of a poly(styrene-co-methyl acrylate) latex (full circles) and in the absence of particles (empty squares). Theoretical predictions of Eq. (12) are given by the full line

the homo-monomer saturation concentrations of the two monomers in the latex of interest the individual monomer concentrations in the latex phase can be calculated from the fraction of monomer in the whole system (with mass balance considerations).

The relationship between the concentration of monomer in the aqueous phase and the droplet phase was shown to obey Henry's law in the presence and absence of latex particles. This was expected, since it has already been shown that Henry's law is obeyed for monomers both in the absence⁹⁾ and presence¹⁰⁾ of latex particles. The presence of a swollen latex particle phase does not influence the monomer partitioning between the droplet and water phases since the monomer ratio in the particle phase is equal to that in the droplet phase for those systems studied in this paper.

Finally, the results of this paper are of considerable importance for the emulsion polymerization field since, if general, they allow simple predictions of both the monomer ratio and concentrations in each of the three phases present during an emulsion polymerization. Although we have endeavored to utilize monomers with different water solubilities, and also in each case varying latex polymer composition, further experimental results are needed to test the limits of the theoretical assumptions utilized in this work. For example, assumption (1) requires that the molar volumes of the two monomers of interest be similar. Although this is usually the case, there are systems where this condition is not met. Further, it must be pointed out that the results of this paper probably only apply to partially water soluble monomers and water insoluble polymers. More complicated expressions for special cases where these conditions are not met have been developed elsewhere³⁻⁵⁾.

The authors would like to thank *Edwin Verdurmen* for a incisive suggestion that sparked the use of approximation (2), and *Harold Schoonbrood* for useful discussions.

¹⁾ E. g. J. Ugelstad, F. K. Hansen, *Rubber Chem. Technol.* **49**, 536 (1976)

²⁾ I. A. Maxwell, B. R. Morrison, R. G. Gilbert, D. H. Napper, *Macromolecules* **24**, 1629 (1991)

³⁾ J. Ugelstad, P. C. Mork, H. R. Mfutakamba, E. Soleimany, I. Nordhuus, R. Schmid, A. Berge, T. Ellingsen, O. Aune, K. Nustad, in *'Science and Technology of Polymer Colloids'*, vol. 1, G. W. Poehlein, R. H. Ottewill, J. W. Goodwin, Eds., *NATO ASI Ser., Ser. E.*, 1983

- ⁴⁾ J. Guillot, *Acta Polym.* **32**, 593 (1981)
- ⁵⁾ C. M. Tseng, M. S. El-Aasser, J. W. Vanderhoff, *Org. Coat. Plast. Chem.* **45**, 373 (1981)
- ⁶⁾ M. Morton, S. Kaizerman, M. W. Altier, *J. Colloid Sci.* **9**, 300 (1954)
- ⁷⁾ P. J. Flory, *'Principles of Polymer Science'*, Cornell University Press, Ithaca, New York 1953
- ⁸⁾ E. Vanzo, R. H. Marchessault, V. Stannett, *J. Colloid. Sci.* **20**, 62 (1965)
- ⁹⁾ J. L. Gardon, *J. Polym. Sci., Polym. Chem. Ed.* **6**, 2859 (1968)
- ¹⁰⁾ I. A. Maxwell, J. Kurja, G. H. J. Van Doremaele, A. L. German, B. R. Morrison, *Makromol. Chem.* **193**, 2049 (1992)
- ¹¹⁾ I. A. Maxwell, A. L. German, to be published