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**Citation for published version (APA):**

Maxwell, I. A., Kurja, J., van Doremaele, G. H. J., German, A. L., & Morrison, B. R. (1992). Partial swelling of latex particles with monomers. *Makromolekulare Chemie*, 193(8), 2049-2063.  
<https://doi.org/10.1002/macp.1992.021930823>

**DOI:**

[10.1002/macp.1992.021930823](https://doi.org/10.1002/macp.1992.021930823)

**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.
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## Partial swelling of latex particles with monomers

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(Date of receipt: September 26, 1991)

### SUMMARY:

Two methods are described for experimentally determining the concentrations of monomer in both the aqueous phase and the latex particle phase during partial swelling of latex particles, and therefore also during interval III of an emulsion polymerization. The ratio of the monomer concentrations in the aqueous phase, both below and at saturation, can be related to the volume fraction of polymer in the latex particles via the Vanzo equation. Comparison of theory and experiments for the methyl acrylate and poly(methyl acrylate-co-styrene) system shows that the monomer partitioning is insensitive to temperature, latex particle radius, polymer composition, polymer molecular weight and polymer cross-linking. Thermodynamic treatment of these and previously published partitioning results shows, at higher volume fractions of polymer, that the conformational entropy of mixing of monomer and polymer is the significant term determining the degree of partial latex particle swelling by monomer. Theoretical predictions of experimental results are quite insensitive to values of the Flory-Huggins interaction parameter and to the latex particle-water interfacial tension. A simple model is developed for the estimation of monomer partitioning which requires only the saturation monomer concentrations in the particle and aqueous phases.

### Introduction

The swelling of polymeric latex particles with solvent and monomer has long been a subject of interest. Early work by Morton et al.<sup>1)</sup> dealt with *saturation* swelling of latex particles, primarily by monomers. However, the *partial* swelling of latex particles by monomers has received less attention. This fact is in contrast with the importance of the so-called interval III of emulsion polymerization, where there are no monomer droplets present, and all monomer is solubilized in both the particle and the aqueous phases. During interval III of an emulsion polymerization the partitioning of monomer between the particle and aqueous phases is a critical factor that may determine, *inter alia*, the rate of polymerization directly, the rate of free-radical exit from latex particles<sup>2)</sup> and the initiator efficiency<sup>3)</sup>, the last two also affecting the rate of polymerization. It should be noted that typical rates of emulsion polymerization are such that thermodynamic equilibrium of monomer between the phases during polymerization is usually achieved. Prediction of the monomer partitioning between the particle and aqueous phases may also aid in the modelling of the kinetics of core shell polymerization in emulsion copolymerization.

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In this paper early work on the partial swelling of latex particles by Vanzo et al.<sup>4)</sup> and Gardon<sup>5)</sup> is reviewed. A series of experimental results on the partitioning of monomers between the aqueous and particle phases are discussed, in which the following variables are systematically changed: latex particle radius, temperature, monomer type, polymer cross-linking density, polymer molecular weight, type and composition of polymer. The observed monomer partitioning results (and previously published data) are compared with predicted results. The purpose of this paper is to find out which thermodynamic factors are important in determining the partitioning of monomer between the aqueous and latex particle phases when there is no separate monomer phase present. This paper will deal exclusively with swelling of latex particles by monomers, but the considerations made are quite general and should apply to most solvents.

### Theory

Morton et al.<sup>1)</sup> considered the saturation swelling of latex particles by solvent having limited solubility in the water phase. When the swollen latex particle 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  $\Delta F$  is the partial molar free energy of monomer,  $\Delta F_m$  the contribution from the energy of mixing of monomer and polymer, and  $\Delta F_s$  the contribution from the particle-water interfacial energy.

Morton et al. expressed the free energy of mixing of monomer and polymer in terms of the classical Flory-Huggins theory<sup>1,6)</sup>:

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

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  $\chi$  the Flory-Huggins interaction parameter.

The interfacial free energy was given in terms of the Gibbs-Thomson equation<sup>7)</sup>

$$\Delta F_s = \frac{2 V_m \cdot \gamma v_p^{1/3}}{R_0} \quad (3)$$

where  $V_m$  is the partial molar volume of the monomer,  $\gamma$  the particle-water interfacial tension and  $R_0$  the unswollen radius of the latex particle.

Combining the terms above gives the so-called Morton equation<sup>1)</sup>:

$$\ln(1 - v_p) + v_p \cdot \left(1 - \frac{1}{\bar{M}_n}\right) + \chi v_p^2 + \frac{2 V_m \cdot \gamma v_p^{1/3}}{R_0 \cdot RT} = 0 \quad (4)$$

Vanzo et al.<sup>4)</sup> were the first to derive an analogue for the Morton equation that dealt with partial swelling of latex particles. Gardon later derived the same expression<sup>5)</sup>. If the latex particles are not saturated by monomer then there is no pure monomer phase present (i. e. no monomer droplets). The partial molar free energy of the monomer in the latex particle phase is then given by<sup>4)</sup>

$$\Delta F = RT \ln a \quad (5)$$

where  $a$  is the activity of the monomer. Vanzo et al. pointed out that the monomer activity can be approximated by  $p/p_0$ , the ratio of the vapor pressure of the monomer at a given volume fraction of polymer ( $p$ ) to the vapor pressure at saturation swelling ( $p_0$ ). Gardon<sup>5)</sup> showed that, since Henry's law holds for latex-free water, the ratio  $p/p_0$  can be approximated by the ratio of the aqueous-phase solubilities of monomer below and at saturation

$$\frac{p}{p_0} = \frac{[M]_{\text{aq}}}{[M]_{\text{aq, sat}}} \quad (6)$$

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

The final result for partial swelling of latex particles by monomer and solvents, hereafter called the Vanzo equation, is<sup>4,5)</sup>:

$$\ln(1 - v_p) + v_p \cdot \left(1 - \frac{1}{\bar{M}_n}\right) + \chi v_p^2 + \frac{2 V_m \cdot \gamma v_p^{1/3}}{R_0 \cdot RT} = \ln \left( \frac{[M]_{\text{aq}}}{[M]_{\text{aq, sat}}} \right) \quad (7)$$

Gardon<sup>5)</sup> derived an expression for the saturation swelling of latex particles composed of densely cross-linked polymer. This theory was an adaption of the Flory-Rehner theory<sup>6)</sup> which describes the free-energy contribution of the elastic energy of the cross-linked polymer network as

$$\frac{\Delta F_e}{RT} = \frac{V_m \cdot d_p}{\bar{M}_c} \left( v_p^{1/3} - \frac{v_p}{2} \right) \quad (8)$$

where  $d_p$  is the density of the polymer, and  $\bar{M}_c$  the mean molecular weight between cross-links. Finally, for the case of partial swelling of latex particles composed of cross-linked polymer we find:

$$\begin{aligned} \ln(1 - v_p) + v_p \cdot \left(1 - \frac{1}{\bar{M}_n}\right) + \chi v_p^2 + \frac{2 V_m \cdot \gamma v_p^{1/3}}{R_0 \cdot RT} + \frac{V_m \cdot d_p}{\bar{M}_c} \left( v_p^{1/3} - \frac{v_p}{2} \right) \\ = \ln \left( \frac{[M]_{\text{aq}}}{[M]_{\text{aq, sat}}} \right) \end{aligned} \quad (9)$$

## Experimental part

### Reagents

Reagent-grade styrene (S) 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. Before use the cross-linking agent ethylene diacrylate (EDA) was washed with a NaOH solution in order to remove inhibitor. The water was distilled twice. Potassium peroxydisulfate (Merck p. a.), dodecanethiol (Merck p. a.) and Aerosol MA80 (sodium dihexyl sulfosuccinate; Cyanamid) 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 copolymerizations containing MA, and at 70 °C for S. 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. For the cross-linked MA seed (MA2) the cross-linking agent (EDA) was added with monomer at the commencement of the seed preparation.

Tab. 1. Seed latex recipes (MA polymerization and copolymerizations at 50 °C; S polymerization at 70 °C)

Non cross-linked seed latex		Cross-linked seed latex	
MA and/or S	30,0 g <sup>a)</sup>	MA	30,0 g <sup>a)</sup>
Water	750,0 g	Water	750,0 g
Potassium peroxydisulfate	0,2 g	Potassium peroxydisulfate	0,2 g
Dodecanethiol	0,3 g <sup>a)</sup>	EDA	1,5 g
Aerosol MA80	2,0 g	Aerosol MA80	2,0 g

a) Unless stated otherwise.

### Particle sizing

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

### Molecular weight determination

The molecular weight of the polymer in seed latices SMA1, SMA2 and SMA4 was controlled by added dodecanethiol in the seed latex recipes (0, 9,6, 0,3 g, respectively). Molecular weight determination of selected seed latices was carried out by size exclusion chromatography (linear  $\mu$ -styragel column thermostated at 313 K; eluent: tetrahydrofuran) utilizing polystyrene standards (this was found to be an adequate method for determining molecular weights of polymers containing MA). The results are listed in Tab. 2.

### Monomer partitioning: centrifuge method

A latex of known solids content and polymer composition was mixed with known amounts of MA in the absence of initiator. The system was allowed to reach equilibrium by shaking (for at least 24 h) while thermostated at the required temperature. The phases (swollen polymer particles

Tab. 2. Seed latex composition, content of polymer solids in the final seed latex (measured by gravimetry), mean radius of the particles and mean degree of polymerization of the polymer

Seed latex	Polymer composition (mole ratio)	Solids content in wt.-%	Unswollen radius in nm	$\bar{M}_n$
SMA1	S:MA (25:75)	16,9	61	15 000
SMA2	S:MA (25:75)	17,3	96	87
SMA3	S:MA (50:50)	14,7	63	—
SMA4	S:MA (25:75)	16,2	48	560
SMA5	S:MA (75:25)	9,0	32	—
SMA6	S:MA (25:75)	16,5	32	—
MA1	MA	12,5	50	15 000
MA2	MA + 5 wt.-% EDA	4,3	65	∞
S1	S	34,3	89	—
VA <sup>a)</sup>	VA	—	≈ 100	—
MMA <sup>b)</sup>	MMA	2,6	65	—
RGM5 <sup>c)</sup>	S	3,6	56	—

a) Ref. <sup>12)</sup>; VA: vinyl acetate.

b) Ref. <sup>16)</sup>; MMA: methyl methacrylate.

c) Ref. <sup>3)</sup>

and aqueous phases) were separated using an ultracentrifuge (Centrikon T-2060) thermostated to the same temperature as above. The concentration of MA in the aqueous phase was determined by gas chromatography (GC) after adding a standard 2-propanol solution in water to a sample of the aqueous phase. The determination of monomer content in the polymer particles was then determined by mass balance. 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. All partitioning experiments were carried out at 45 °C unless otherwise stated.

#### *Monomer partitioning: dialysis method*

The reliability of the above method was confirmed by means of additional monomer partitioning experiments using common dialysis tubing for the separation of the latex and aqueous phases. GC analysis of the aqueous phase was conducted by the same method as described in the previous paragraph. The results obtained for the two methods were in excellent accord (Fig. 1). It was also noted that phase equilibrium was always achieved within 30 min.

#### *Saturation concentration of MA in the aqueous phase*

The effect of surfactant concentration upon the saturation concentration of MA in the aqueous phase at various temperatures was investigated. MA was mixed with water containing various concentrations of surfactant (sodium dodecyl sulfate, SDS). GC analysis of the aqueous phase was carried out as above. It was found (Fig. 2) 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 ascribed to stronger hydrogen bonding at lower temperatures.

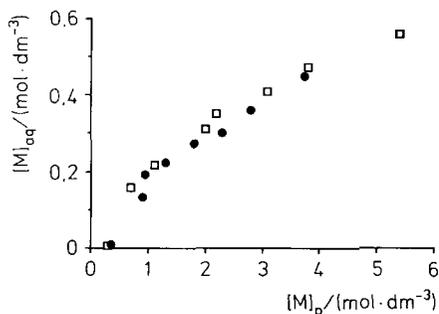


Fig. 1. Comparison of two methods, the ultracentrifuge method (empty squares) and dialysis method (full circles), for measuring the concentration of MA in the aqueous phase ( $[M]_{aq}$ ) and in the latex particle phase ( $[M]_p$ ) at 45 °C

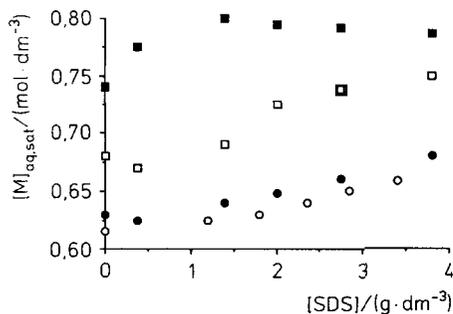


Fig. 2. Experimentally determined saturation concentrations of MA in water as a function of SDS concentration at 4 °C (full squares), 20 °C (empty squares), 35 °C (full circles) and 45 °C (empty circles)

## Results and discussion

### Swelling with methyl acrylate (MA)

#### Influence of particle size

Experiments were performed to determine the MA partitioning between latex particles and aqueous phase, for latex particles differing only by particle size. The three seed latices used (SMA6, SMA1, SMA2) all have similar copolymer composition, polymer solids and surfactant type, although they differ in nominal polymeric molecular weight (it will be shown below that this last point does not change the conclusions of this section). Further, each of the seeds was found to have less than 1 g/dm free surfactant in the aqueous phase. It has been found<sup>8)</sup> that latices of differing sizes with similar polymer composition, surfactant and surfactant coverages have similar interfacial tensions at a particular fraction of polymer. Hence, in the experiments described in this section it was thought that the interfacial tension at a particular fraction of polymer for all three latices would be approximately the same.

The partitioning results for MA with the three different particle sizes are displayed in Fig. 3. The most significant result of these experiments is the small effect of the differing particle sizes. It is apparent that the interfacial free energy has little effect upon the partitioning of monomer. To emphasize this point, in Fig. 4 the predicted con-

tribution of all three terms in Eq. (7) (the Vanzo equation) are displayed individually for seed SMA6 ( $R_0 = 32$  nm): these terms are the conformational entropy of mixing of polymer and solvent ( $\Delta F_m$  (conformational)/(RT) =  $\ln(1 - v_p) + v_p$ , derived<sup>6</sup> by considering the entropy of mixing of an assembly of random-flight chain molecules with solvent), the ‘residual’ free energy term ( $\Delta F_m$  (residual)/(RT) =  $\chi v_p^2$ , containing both enthalpic and entropic terms) and the interfacial free-energy term ( $\Delta F_s$ /(RT) =  $2 V_m \cdot \gamma v_p^{1/3}/(R_0 \cdot RT)$ ). It is possible that both the interaction parameter and the interfacial tension change with volume fraction polymer. However, an estimate of the interaction parameter can be made from the high-volume-fraction polymer data, where the contribution to the degree of swelling of the interfacial free energy is least (this point is realized by the converging curves in Fig. 3 at high volume fraction). Assuming, at these high volume fractions of polymer, that  $\gamma = 0$  for all three latices we find from fitting Eq. (7) to the data that  $\chi = 0,2$ . Further, the saturation swelling of the latex particles is limited by the interfacial tension, and at these conditions the Morton equation (a limit of the Vanzo equation) is most sensitive to the value of the interfacial tension. Assuming that the above calculated value of the interaction parameter is valid at lower volume fraction from the saturation swelling of seed SMA6 we find via Eq. (7)  $\gamma = 45 \text{ dyn} \cdot \text{cm}^{-1}$  (1 dyn =  $10^{-5}$  N). Inserting these values for the interaction parameter and the interfacial tension into the Vanzo equation we find excellent agreement of theory and experiment (Fig. 4).

Fig. 3. Comparison of the experimentally measured monomer partitioning of MA at 45 °C for three seed latices differing only by their mean unswollen particle radii,  $R_0 = 32$  nm (empty circles), 61 nm (empty squares) and 96 nm (full circles);  $v_p$ : volume fraction of polymer in the latex particles

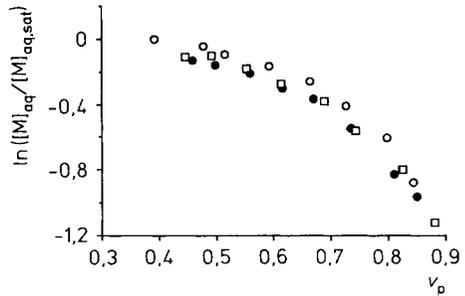
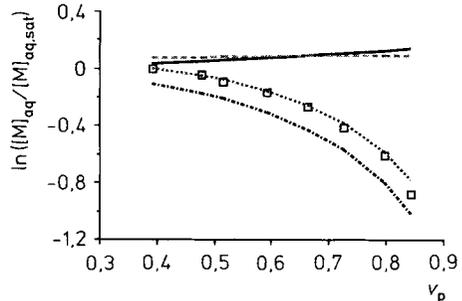


Fig. 4. Comparison of theoretical predictions and experimental measurements of MA partitioning at 45 °C for seed latex SMA6.

Theoretical predictions:  
 conformational entropy term given by  $\ln([M]_{aq}/[M]_{aq,sat}) = \ln(1 - v_p) + v_p$  (· · · ·); residual free energy term given by  $\ln([M]_{aq}/[M]_{aq,sat}) = \chi v_p^2$ , with  $\chi = 0,2$  (—); interfacial free energy term given by  $\ln([M]_{aq}/[M]_{aq,sat}) = 2 V_m \cdot \gamma v_p^{1/3}/(R_0 \cdot RT)$ , with  $\gamma = 45 \text{ dyn} \cdot \text{cm}^{-1}$  (---); and Vanzo equation (Eq. (7)) with  $\chi = 0,2$  and  $\gamma = 45 \text{ dyn} \cdot \text{cm}^{-1}$  (· · · ·)



From this series of experiments we can state that the major contribution to the limit of partial swelling of latex particles by monomer is the partial molar free energy associated with the conformational entropy of mixing of monomer and polymer. The residual free energy of mixing (the term including the interaction parameter) and the partial molar interfacial free energy do not make a significant contribution at higher volume fractions of polymer in the latex particles. Of course, as saturation swelling is approached the contributions of both latex particle interfacial free energy and the residual free energy become more important.

### Influence of temperature

Monomer partitioning experiments were undertaken with seed SMA4 at two different temperatures (20 °C and 45 °C). The saturation concentrations of MA in the seed SMA4 was found to be temperature-independent at 20 °C and 45 °C (the error in these measurements was calculated to be ca. 3%). The saturated aqueous-phase concentrations of MA were found to be 0,68 mol/dm (20 °C) and 0,63 mol/dm (45 °C). Within experimental error temperature had no effect upon the partitioning of MA (Fig. 5). The temperature independence of the partitioning results can be partially understood since the partial molar free energy of the interface is unlikely to change considerably over the temperature range studied. However, it is not known how the Flory-Huggins interaction parameter would change with temperature for this polymer-monomer system, since  $\chi$  as defined contains both temperature-dependent enthalpic terms and temperature-independent entropic terms. Despite this, the temperature independence of the partitioning results is expected since we have shown that the major contribution to the partial molar free energy of monomer is the conformational entropy term of the free energy of mixing of monomer and polymer. Accordingly, the Vanzo equation with a single value of the interaction parameter, and also of the interfacial tension (both these values independently found in the previous section) provide excellent predictions of the results at 20 °C and 45 °C (Fig. 5).

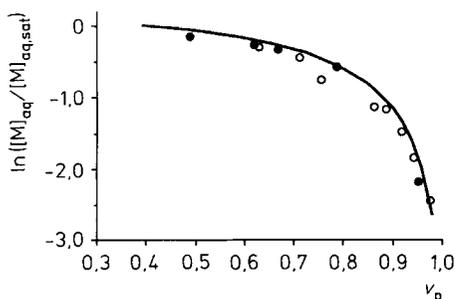


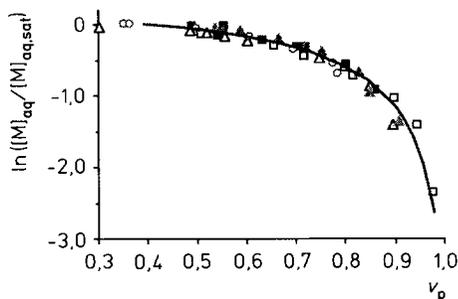
Fig. 5. Comparison of the experimentally measured monomer partitioning of MA for seed latex SMA4 at 20 °C (empty circles) and 45 °C (full circles). Theoretical line: Vanzo equation (Eq. (7)) with  $R_0 = 48$  nm,  $\chi = 0,2$  and  $\gamma = 45$  dyn · cm<sup>-1</sup>

### Influence of copolymer composition

In the previous section it was shown that temperature has little effect on monomer partitioning below saturation swelling. In this section the effect of the residual free

energy of mixing on the partitioning of MA is examined by swelling particles of different copolymer composition. It is thought that the interaction parameter for the MA-polymer systems will vary considerably for polystyrene and poly(methyl acrylate); and also for different compositions of copolymers containing these two polymers. The results of these experiments are displayed in Fig. 6 together with the predictions of the Vanzo equation with values of the interaction parameter and interfacial tension fitted above. It is obvious that the polymer composition has little effect upon the partitioning of MA in these seed latices. Although we might expect the value of the interaction parameter to change for MA-polymer systems with differing polymer composition, the main contribution to the partitioning appears to be the conformational entropy of mixing of monomer and polymer, and hence we see little variation in the partial swelling of different seed latices with the one monomer.

Fig. 6. Comparison of the experimentally measured monomer partitioning of MA at 45 °C for five seed latices differing by their polymer composition: S1 (mole ratio S:MA 100:0) (full triangles), SMA5 (75:25) (empty squares), SMA3 (50:50) (full squares), SMA1 (25:75) (empty triangles), MA1 (0:100) (empty circles). Theoretical line: Vanzo equation (Eq. (7)) with  $R_0 = 35$  nm,  $\chi = 0,2$  and  $\gamma = 45$  dyn · cm<sup>-1</sup>



#### Influence of molecular weight

Three seed latices were prepared with significantly different average degrees of polymerization,  $\bar{M}_n = 87$  (SMA2),  $\bar{M}_n = 560$  (SMA4) and  $\bar{M}_n = 15\,000$  (SMA1). The partitioning results for MA between the polymer and aqueous phases for these three latices are displayed in Fig. 7. It is apparent that the partitioning of MA is not affected by the differing molecular weights. The reciprocal of the average degree of polymerization of the lowest-molecular-weight polymer utilized,  $\bar{M}_n = 87$ , is considerably smaller than unity, and therefore has negligible effect upon the entropy of mixing (i. e.  $v_p \cdot (1 - 1/\bar{M}_n) \approx v_p$ ). These results are in accord with what would be expected from theoretical considerations (Fig. 7), since we have already found that the conformational entropy term dominates the partitioning, and that the conformational-entropy free-energy term in the Vanzo equation does not predict change in the partitioning of MA over the range of molecular weights of polymer utilized.

#### Influence of cross-linking density

The partitioning of MA between the particle and aqueous phases for a latex made with 5 wt.-% EDA ( $\bar{M}_c \approx 1\,000$ ) is compared with the MA partitioning in an uncross-linked latex (Fig 8). Again, there is no difference in the partitioning between these two polymer latices. This is simply because the free energy due to the conformational

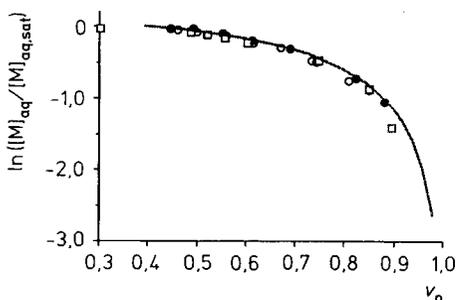


Fig. 7. Comparison of the experimentally measured partitioning of MA at 45 °C for three latices differing by their polymer molecular weight:  $\bar{M}_n = 87$  (SMA2) (empty circles), 560 (SMA4) (empty squares) and 15 000 (SMA1) (full circles). Theoretical line: Vanzo equation (Eq. (7)) with  $\bar{M}_n = 87$ ,  $R_0 = 35$  nm,  $\chi = 0,2$  and  $\gamma = 45$  dyn  $\cdot$  cm $^{-1}$

entropy of mixing of monomer and polymer dominates the thermodynamics of monomer partitioning. It was expected from numerical calculations utilizing Eq. (9) that the measured cross-linking density would have no effect upon the monomer partitioning (Fig. 8).

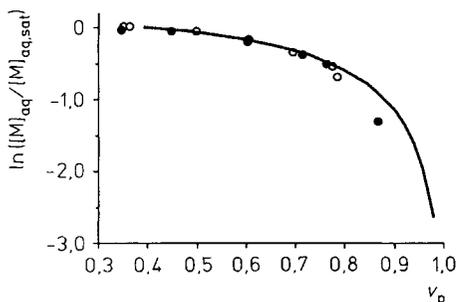


Fig. 8. Comparison of the experimentally measured partitioning of MA at 45 °C for two latices differing by their degree of cross-linking: uncross-linked (MA1) (empty circles), 5 wt.-% cross-linking agent (MA2) (full circles). Theoretical line: Eq. (9) with  $\bar{M}_c = 1\,000$ ,  $R_0 = 50$  nm,  $\chi = 0,2$  and  $\gamma = 45$  dyn  $\cdot$  cm $^{-1}$

### Other monomer partitioning results

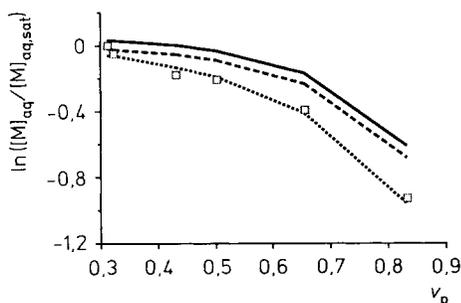
There are many references to the partitioning of monomers between the latex particle and aqueous phases. With the exception of the two early papers on the subject<sup>4,5</sup>, most workers have fitted their partitioning data to empirical formulae. In this section we reinterpret some of these literature results in terms of the Vanzo equation.

### Styrene in polystyrene

Maxwell et al.<sup>3</sup> measured the partitioning of styrene between the aqueous phase and a polystyrene latex at 50 °C. For this system it is known<sup>8</sup> that  $\chi \approx 0,4$ . In Fig. 9 the experimental results for this system are compared with the theoretical predictions for values of the interfacial tension,  $\gamma = 0$  and 20 dyn  $\cdot$  cm $^{-1}$  (a typical range for latex particles) and values of the interaction parameter of  $\chi = 0$  and 0,4. It is apparent that the best fit to the data is with  $\chi = 0$  and  $\gamma = 0$  dyn  $\cdot$  cm $^{-1}$ . This indicates that the only significant free-energy contribution to monomer partitioning is the conformational entropy of mixing of styrene and polystyrene. This is in contrast to those results for MA described in this paper, where, although the conformational entropy of mixing of

monomer and polymer was the dominant term, there was always a small contribution from the interfacial free energy and the residual free energy of mixing. However, it must be pointed out that there is much greater scope for experimental error in the measurement of styrene concentrations in the aqueous phase by GC, simply because of the low concentrations involved. Gardon<sup>5)</sup> earlier found similar results for the partitioning of styrene in a polystyrene latex at 40 °C. Gardon did not comment on the deviation of experimental results from the theoretical prediction. It is difficult to speculate on the cause of these deviations. However, it is realized that polystyrene latices made with Aerosol MA80 may have low interfacial tensions, since this would explain the saturation concentration of styrene in these particles: at 50 °C it is found<sup>9)</sup> that the saturation concentration of styrene in monodisperse ( $R_0 = 56$  nm) polystyrene seed latex particles is  $[M]_p = 5,8$  mol/dm. Assuming that the Morton equation<sup>1)</sup> properly describes saturation swelling of latex particles, this would suggest a low value of the interfacial tension,  $\gamma < 5$  dyn · cm<sup>-1</sup>. Secondly, the value of the interaction parameter measured by Tseng et al.<sup>8)</sup>,  $\chi = 0,4$ , depends critically upon the experimentally measured interfacial tension, which was determined by assuming that the water-particle interfacial tension could be approximated by the monomer droplet-particle interfacial tension measured by the drop-volume method. It is hard to assess the validity of this method, but there is certainly some error involved. However, the value of the above measured interaction parameter ( $\chi = 0,4$ ) does correspond well to values measured for the solution of polystyrene in toluene (a solvent similar to styrene) at the same temperature<sup>10)</sup>. Clearly, further experimental evidence is required before the nature of the residual free-energy term for this system is deduced.

Fig. 9. Comparison of theoretical predictions and experimental measurements<sup>3)</sup> of styrene partitioning at 50 °C for a polystyrene seed latex RGM5. Theoretical predictions with Vanzo equation (Eq. (7)):  $\chi = 0,4$ ,  $\gamma = 20$  dyn · cm<sup>-1</sup> (—);  $\chi = 0,4$ ,  $\gamma = 0$  dyn · cm<sup>-1</sup> (- - -);  $\chi = 0$ ,  $\gamma = 0$  dyn · cm<sup>-1</sup> (· · ·); experimental points (empty squares)



#### Vinyl acetate in poly(vinyl acetate)

Vanzo et al.<sup>4)</sup> measured the partitioning of vinyl acetate between the aqueous and poly(vinyl acetate) particle phases. However, these workers utilized sodium dodecyl sulfate (SDS) concentrations that, although stated to be below the critical micelle concentration (CMC), were in fact above it. For example, 0,4 wt.-% SDS solution in water is approximately twice the CMC for SDS in pure water<sup>11)</sup>. Furthermore, in the presence of solvents and monomers the CMC for SDS is known to be depressed<sup>11)</sup>. Therefore the interpretation of the results of Vanzo et al. are complicated by the likely presence of a separate monomer droplet (swollen micellar) phase.

The partitioning of vinyl acetate between the aqueous and poly(vinyl acetate) latex phases has been measured<sup>12, 13, 14)</sup> at various temperatures. The results of Napper and Parts<sup>12)</sup> at 40 °C are compared to theoretical predictions in Fig. 10. The value of the interaction parameter utilized in the theoretical calculations was  $\chi = 0,41$ , measured<sup>15)</sup> for the vinyl acetate-poly(vinyl acetate) system at a volume fraction of polymer  $v_p = 0,4$  and at 30 °C. Once more it is apparent that within experimental error all the theoretical predictions are consistent. Because of the insensitivity to  $\chi$  and  $\gamma$  of the fits of the Vanzo equation to experiment we have refrained from, say, fitting these two parameters by a non-linear least-squares fitting technique. The insensitivity to these parameters is a result of both the conformational entropy of mixing dominating the partial molar free energy of the monomer and also the uncertainty in the experimental data. It should also be noted that both the interaction parameter and the interfacial tension may be dependent on the volume fraction of polymer, and this would introduce, at least, four adjustable parameters into any fit to the data. Finally, Netschey and Alexander<sup>14)</sup> found partitioning results that were not in agreement with other data<sup>12, 13)</sup>. New experimental data may be needed before further comparisons of theory and experiment for this system are undertaken.

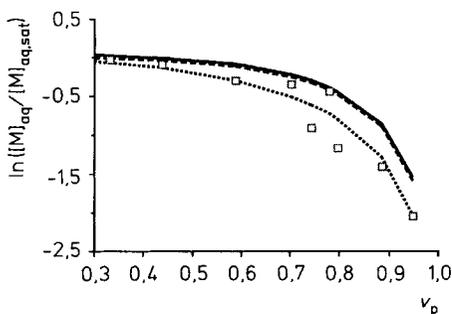
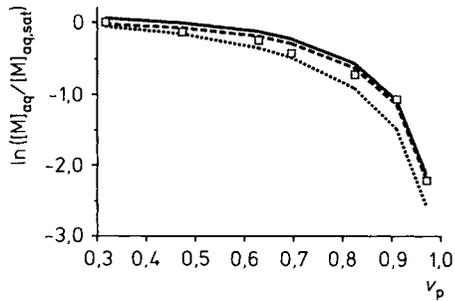


Fig. 10. Comparison of theoretical predictions and experimental measurements<sup>12)</sup> of vinyl acetate partitioning at 40 °C for a poly(vinyl acetate) seed latex. Theoretical predictions with Vanzo equation (Eq. (7)):  $\chi = 0,41$ ,  $\gamma = 50$  dyn · cm<sup>-1</sup> (—);  $\chi = 0,41$ ,  $\gamma = 0$  (---);  $\chi = 0$ ,  $\gamma = 0$  (· · ·); experimental points (empty squares)

#### Methyl methacrylate in poly(methyl methacrylate)

Ballard et al.<sup>16)</sup> measured the partitioning of methyl methacrylate (MMA) between the aqueous phase and a poly(methyl methacrylate) latex at 50 °C. For this system values of the interaction parameter between  $\chi = 0,29$  and  $0,42$  have been suggested<sup>8)</sup> (although these authors<sup>8)</sup> did not consider any polymer volume fraction dependence of the interaction parameter). Theoretical predictions of the partitioning are displayed in Fig. 11, calculated with a value of the interaction parameter of  $\chi = 0,5$  (this large value should maximize any effect of the interaction parameter on the calculated partitioning). It is apparent that, within experimental error, it is impossible to assign values to the interaction parameter, nor to the interfacial tension. However, we can state that the Vanzo equation provides a good description of the monomer partitioning between the two phases, and that the dominant term is that due to the conformational entropy of mixing of monomer and polymer.

Fig. 11. Comparison of theoretical predictions and experimental measurements<sup>16</sup> of methyl methacrylate partitioning at 50°C for a poly(methyl methacrylate) seed latex. Theoretical predictions with Vanzo equation (Eq. (7)):  $\chi = 0,5, \gamma = 50 \text{ dyn} \cdot \text{cm}^{-1}$  (—);  $\chi = 0,5, \gamma = 0$  (- - -);  $\chi = 0, \gamma = 0$  (· · ·); experimental points (empty squares)



*Estimation of monomer partitioning*

The monomer partitioning between the aqueous and latex particle phases can be predicted from the complete Vanzo equation (Eq. (7)). However, this requires that both the interaction parameter and the interfacial tension be known. A further complication already mentioned is that both these parameters may be polymer volume fraction dependent. Also, values of these parameters are difficult to determine by independent experiments. With these complications in mind there are at least two possible approaches for the estimation of monomer partitioning: (a) First, the approach described above can be utilized. That is, an estimate of the interaction parameter can be made from partitioning results at high volume fractions of polymer in the latex particles, since the contribution of the interfacial tension to the Vanzo equation is least at high fraction of polymers. Then, from saturation swelling results a value of the interfacial tension can be estimated by fitting of the Morton equation. For the MA-poly(methyl acrylate-co-styrene) system this technique provides excellent agreement between prediction and experiment (Figs. 4–8). However, it requires that partitioning results be determined experimentally. (b) Another, more empirical approach, is to estimate the value of the sum of the residual free energy and the particle-water interfacial free-energy terms in the Vanzo equation from the saturation swelling volume fraction of polymer. This can be done by utilizing the Morton equation: We calculate a correction term

$$\text{corr.} = -[\ln(1 - v_{p, \text{sat}}) + v_{p, \text{sat}}] \tag{10}$$

where  $v_{p, \text{sat}}$  is the volume fraction of polymer in the latex particles at saturation swelling by monomer. Then we can utilize this correction term in the Vanzo equation:

$$\ln(1 - v_p) + v_p + \text{corr.} = \ln \left( \frac{[M]_{\text{aq}}}{[M]_{\text{aq}, \text{sat}}} \right) \tag{11}$$

Note that, for simplicity, we have ignored the contribution of polymer molecular weight upon the partial molar free energy of mixing of monomer and polymer in Eqs. (10 and 11) (i. e.  $\bar{M}_n \gg 1$ ). The approach used to derive Eq. (11) incorrectly assumes that both the interfacial free-energy and the residual free-energy term are independent of the volume fraction of polymer. However, since the absolute values of

these terms are small compared to the conformational-entropy term, this approach, as a first estimate, gives quite good results for the MA-poly(methyl acrylate-co-styrene) system (Fig. 12). Comparison of the predictions of Eq. (11) with more experimental results are needed before complete confidence can be expressed in this approach. It is important to note that the only parameters needed to predict the partial monomer partitioning between the latex particle and aqueous phases by this approach are the saturation concentrations of monomer in the particle and aqueous phases.

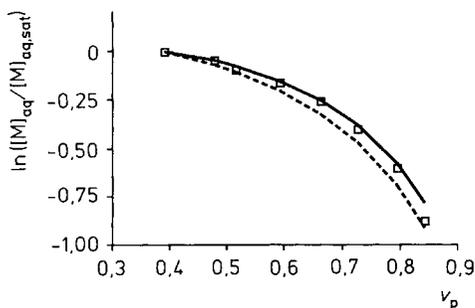


Fig. 12. Comparison of theoretical predictions and experimental measurements of MA partitioning at 45 °C for latex SMA6. Theoretical predictions with Vanzo equation ( $\chi = 0,2$  and  $\gamma = 45 \text{ dyn} \cdot \text{cm}^{-1}$ ) (—) and Eq. (11) (corr. = 0,1) (---)

## Conclusions

The major results of this work are: (1) The Vanzo equation successfully models the partitioning of monomer between the aqueous phase and the latex particle phase in the absence of a separate monomer phase. (2) For the systems studied (styrene, methyl acrylate, vinyl acetate and methyl methacrylate with a variety of polymer latices) the contribution of the conformational entropy of mixing of monomer and polymer dominates the free energy of mixing at higher volume fraction of polymer which are typical within latex particles ( $v_p \approx 0,3 - 1$ ). (3) The interfacial free energy does not contribute greatly to those parameters that determine the degree of *partial* latex particle swelling. This is in contrast to the *saturation* swelling of latex particles where the balance between the free energy associated with the mixing of monomer and polymer and the free energy of the particle-water interface determines the degree of latex particle swelling. It should be noted that as saturation swelling is approached both the residual free-energy and interfacial free-energy terms in the Vanzo equation become more important.

The Flory-Huggins theory works very well for the partial swelling of latex particles for the following reasons: (1) The polymer concentrations within latex particles are always relatively high. Therefore there should be a uniform density of Flory-Huggins segments. (2) The residual-energy term (the  $\chi$  term) is not a major contributor to the thermodynamic problem at the higher volume fraction of polymers. Hence all the uncertainties associated with the measurement and interpretation of the interaction parameter are less consequential. As pointed out by Flory<sup>6)</sup> the original derivation of the Flory-Huggins theory resulted in an interaction parameter that should be polymer-concentration dependent at high volume fraction of polymer. This is not a problem for the experimental systems studied in this work since within experimental error the fit of the Vanzo equation to experimental data was insensitive to the value of the interaction

parameter (within reasonable bounds). The Flory-Huggins term that describes the conformational entropy of mixing of monomer and polymer is very successful at predicting the monomer partitioning. This entropic term was also derived by Hildebrand<sup>17)</sup> via a free-volume approach and is probably quite general.

For the partitioning of MA it was found that the following variables had little or no effect upon the experimental results: latex particle radius, temperature, polymer cross-linking density, polymer molecular weight, polymer type and polymer composition. All these results agree well with theoretical predictions. For those results extracted from the literature the theoretical predictions also gave satisfactory results, except for the styrene system where anomalously low values for the interfacial tension and interaction parameter were needed to obtain a good fit to the data. However, considering the probable error and the scatter in these data, it is not believed that too much importance can be attached to these relatively small deviations. Further experimental results are needed to determine the cause of these variations.

Finally, the partitioning of monomer between the aqueous and latex particle phases when there is no separate monomer phase present can be predicted accurately if both the interaction parameter and interfacial tension are known. Both of these parameters are possibly polymer concentration dependent (in the case of the interfacial free energy this may be due to the monomer concentration at the interface). This fact, combined with the typical experimental uncertainties, makes any prediction of these parameters from fits of the Vanzo equation to experimental data an unfavorable technique. However, if these parameters are not known then the partitioning can be well estimated by utilizing the entropy of mixing term in the Vanzo equation along with a correction term (Eqs. (10) and (11)) calculated from a fit of the Morton equation to saturation swelling data. In this case, prediction of the partial monomer swelling of latex particles requires only that the values of the saturation concentrations of the monomer in the particle and aqueous phases be known.

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