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Thermodynamics of monomer partitioning in polymer latices:
effect of molar volume of the monomers

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Introduction

Recently a number of papers have appeared on the thermodynamics of monomer partitioning of moderately water-soluble monomers in polymer latex systems. In these papers a very straightforward model was given and this was compared with a broad range of experimental data. One of the basic assumptions in this model was that for most common monomers the molar volumes can be assumed to be similar. In addition to a sensitivity analysis published earlier, this work is intended to elaborate more on deviations that occur when the molar volumes of the monomers are not similar. Experimental data are shown for two monomers with different molar volumes.

Results and discussion

The equations that were used to describe the monomer partitioning behaviour are the following (valid for two monomers, but in principle easily adjustable to describe \( n \) monomers):

\[
\frac{\Delta F_{ip}}{RT} = \ln v_{ip} + (1 - m_{ij}) v_{jp} + v_p + x_{ij} \cdot v_p^2 + x_{ip} \cdot v_p^2 + v_{jp} \cdot v_p (x_{ij} + x_{ip} - x_{jp} \cdot m_{ij}) + \frac{2y V_i}{rRT}
\]

(1a)

\[
\frac{\Delta F_{id}}{RT} = \ln v_{id} + (1 - m_{ij}) v_{jd} + x_{ij} \cdot v_{jd}^2
\]

(1b)

\[
\frac{\Delta F_{iaq}}{RT} = \ln \left( \frac{C_{iaq}}{C_{iaq,s,h}} \right)
\]

(1c)

where \( v_{ip}, v_{id} \) are the volume fractions of monomer \( i \) in the polymer and droplet phase, \( m_{ij} \) is the ratio of the molar volumes of monomers \( i \) and \( j \), \( x_{ij} \) is the Flory-Huggins interaction parameter between monomers \( i \) and \( j \), \( x_{ip} \) is the interaction parameter between monomer \( i \) and polymer, \( C_{iaq} \) is the concentration of monomer \( i \) in the aqueous phase and \( C_{iaq,s,h} \) its saturation value if there are no other monomers present; \( y \) is the interfacial tension between the aqueous and polymer phases, \( V_i \), molar volume of monomer \( i \), and \( r \) is the swollen radius of the polymer particles.

The basic assumptions that led to major simplifications are:

1. the ratio of the molar volumes, \( m_{ij} \), can be set equal to 1.
(2) the contributions of the enthalpy of mixing and the conformational entropy of mixing to the partial molar free energy of mixing two monomers in the monomer or droplet phase, i.e., the third term on the right-hand side of Eq. (1b), are negligible compared to all other terms.

(3) for the contributions of enthalpy and conformational entropy to the partial molar free energy of mixing of the monomers with the polymer in the particles one can assume the interaction parameters for monomer with polymer to be equal for each monomer. The contribution of enthalpy and conformational entropy to the mixing of the two monomers in the particles, represented by $\chi_{ij}$, can be assumed to be negligible, as with the mixing of the monomers by themselves in the droplet phase.

Under saturated conditions these assumptions lead to the following equations:

\[
\begin{align*}
  f_{id} &= \frac{\Delta F_{id}}{RT} = \ln f_{id} \\
  C_{i_{aq}} &= f_{ip} \cdot C_{i_{aq},s,h}
\end{align*}
\] (2a)

where $f_{ip}, f_{id}$ are the mole fractions of monomer $i$ in the polymer phase, resp., the droplet phase. The reader is referred to refs.1-3) for a more detailed treatment.

Regarding this model we note the following:

i) It can be argued that Eq. (1b) might have to be replaced by Eq. (3):

\[
\Delta F_{id} = \ln f_{id}
\] (3)

Eq. (3) is the simplest representation of mixing of two low molecular weight compounds. However, the use of this equation instead of Eq. (1b) will have no effect on the resulting equations if $m_{ij} = 1$.

ii) In the sensitivity analysis that was performed6), only the monomer droplet phase and the polymer phase were considered (i.e., Eq. (2a)). It was shown that large deviations of $m_{ij}$ from 1 (e.g. $m_{ij} = 0,1$), when applying the full equations Eq. (1a) and Eq. (1b), did not result in large deviations from the prediction of Eq. (2a). These deviations are certainly not larger than the experimental uncertainty. The thermodynamic behaviour of the aqueous phase is very different from both other phases (in the aqueous phase the monomers do not influence each other, as this phase is normally very dilute; in the other phases the monomers have a large influence upon each other). The fact that $m_{ij} \neq 1$ should not have any effect on the thermodynamic behaviour of the monomers in the aqueous phase. The effect of $m_{ij}$ not being equal to 1 has comparable effects on the concentrations in the droplet and polymer phases, and therefore Eq. (2a) can still be used. However, if one is to compare droplet phase and aqueous phase, the effect of $m_{ij}$ might be noticeable.

Taking the above two points into consideration we did some simple calculations to show that $m_{ij}$ has a significant effect when comparing the droplet phase and the aqueous phase. For saturated conditions, the following three different equations were used for the evaluation of $\Delta F_{id}/(RT)$:
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\[ \frac{\Delta F_{id}}{RT} = \ln v_{id} \]  \hspace{1cm} (4a)

\[ \frac{\Delta F_{id}}{RT} = \ln f_{id} \]  \hspace{1cm} (4b)

\[ \frac{\Delta F_{id}}{RT} = \ln v_{id} + (1 - m_{ij}) v_{jd} \]  \hspace{1cm} (4c)

and Eq. (1 c) was used for the aqueous phase.

\[ \frac{C_{iaq}}{C_{iaq,s,h}} \]  was calculated by equating Eq. (1 c) to Eqs. (4a), (4b) and (4c), respectively, whilst \( m_{ij} \) was varied (Figs. 1a und b).

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**Fig. 1a.** Ratio of concentration of monomer \( i \) in the aqueous phase and its saturation value \( \frac{C_{iaq}}{C_{iaq,s,h}} \) vs. volume fraction of monomer \( i \) in droplet phase \( v_{id} \) calculated with the ratio of molar volumes of monomers \( i \) and \( j \) \( m_{ij} = 0.5 \) according to Eq. (4a) (full line), Eq. (4b) (dashed line) and Eq. (4c) (dotted line)

**Fig. 1b.** Ratio of concentration of monomer \( i \) in the aqueous phase and its saturation value \( \frac{C_{iaq}}{C_{iaq,s,h}} \) vs. volume fraction of monomer \( i \) in droplet phase \( v_{id} \) calculated with the ratio of molar volumes of monomers \( i \) and \( j \) \( m_{ij} = 0.25 \) according to Eq. (4a) (full line), Eq. (4b) (dashed line) and Eq. (4c) (dotted line)
It can be easily seen that the value of $m_{ij}$ has a significant effect on the concentrations in the aqueous phase, certainly a much more significant effect than was found for the comparison of the droplet and polymer phases. To compare these calculations with experimental data we did some experiments with methyl acrylate (MA) and cyclohexyl methacrylate (CHMA), for which $m_{MA-CHMA} = 0.515$. In Fig. 2 we plotted the experimental values of $C_{MA_{aq}}/C_{MA_{aq,s}}$ versus the experimental $v_{MA_d}$. We also indicated the predictions according to Eqs. (4a–c) with $m_{ij} = m_{MA-CHMA} = 0.515$. The use of Eq. (4a) is certainly not valid. The predictions by Eqs. (4b) and (4c) are in good agreement with the experimental data. Based on these results it seems justifiable to use either Eq. (4b) or Eq. (4c) when $m_{ij} \neq 1$. But since the predictions of both equations are so close, we cannot discriminate between either equation. To find out what equation should be applied at higher values of $m_{ij}$, experiments with other monomers could perhaps give an answer. It should be noted that in most practical systems, Eq. (4b) will be valid, as cases where $m_{ij} < 0.5$ will be rare.

Fig. 2. Experimental data of the ratio of concentrations of methyl acrylate in the aqueous phase and its saturation value $C_{MA_{aq}}/C_{MA_{aq,s}}$ vs. volume fraction of methyl acrylate in droplet phase $v_{MA_d}$, and the predictions with ratio of molar volumes of methyl acrylate and cyclohexyl methacrylate $m_{MA-CHMA} = 0.515$ according to Eq. (4a) (full line), Eq. (4b) (dashed line) and Eq. (4c) (dotted line)

In addition we analysed the polymer phase (the polymer phase was a polystyrene latex with a particle diameter of 86.6 nm (transmission electron microscopy)) in the same system, and the results are displayed in Figs. 3a and 3b. The data in Fig. 3a unambiguously show the validity of Eq. (2a). For the total monomer concentrations in the polymer phase, the following equation was experimentally derived by Maxwell et al.:

$$C_{p,s} = f_{ip} \cdot C_{ip,s,h} + f_{jp} \cdot C_{jp,s,h}$$  \hspace{1cm} (5a)

$$C_{ip} = f_{ip} \cdot C_{p,s}$$  \hspace{1cm} (5b)
Fig. 3a. Experimental data of mole fraction of methyl acrylate in polymer phase $f_{MA,p}$ vs. mole fraction of methyl acrylate in droplet phase $f_{MA,d}$ and the prediction according to Eq. (2a)

Fig. 3b. Experimental data for the concentrations in the polymer phases ($C_p$) for methyl acrylate $C_{MA,p}$ (●), cyclohexyl methacrylate $C_{CHMA,p}$ (○) and total concentration $C_{p,s}$ (□). The straight line is a fit to the data of $C_{p,s}$, the other lines are predictions according to Eq. (5b)

where $C_{p,s}$ is the total monomer concentration in the polymer phase, and $C_{ip,s,h}$ the saturation concentration of monomer $i$ in the absence of any other monomer. The data for $C_{p,s}$ in Fig. 3b were fitted to a straight line, and the fit is satisfactory. This fit gives the values for $C_{ip,s,h}$ which were used with Eqs. (5a) and (5b) to give predictions for the values of $C_{ip}$. The predictions are in excellent accord with the data.

Conclusions

Up until now the comonomer systems that were used to check Eqs. (2a), (2b), (5a) and (5b) all complied with $m_{ij} = 1$. The data presented in this work indicate that these equations can still be used with systems where $m_{ij}$ deviates from 1, at least up to a value of 2 (with the notion that for the droplet phase mole fractions should be used rather than volume fractions).
Experimental part

A polystyrene latex was mixed with the monomers (methyl acrylate (Aldrich) and cyclohexyl methacrylate (Scientific Polymer Products)) and left to stand overnight to equilibrate. This mixture was then transferred to tubes, which were placed in a Sorvall OTD-65 ultracentrifuge (5 h at 50000 r.p.m.) to obtain phase separation. For analysis of the phases a HP 5890 gas chromatograph was used. Butyl acrylate was used as an internal standard.

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