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Partition Coefficients in Latex Systems: Experimental Determination and Modeling

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ABSTRACT: A differential pressure technique was developed to specify the monomer partitioning coefficients in latex systems at monomer concentrations up to saturation. Differential pressures were measured on addition of the monomer either to water or to latex. Distribution of monomers between the polymer-particles and aqueous phase was determined using both experimental data sets. Partition coefficients of vinyl acetate and butyl acrylate in the latexes based mainly on the corresponding monomers were evaluated at 65 °C. The data were correlated by a new model considering the thermodynamic equilibrium between two liquid phases of the latex system. Monomer activity in the polymer-particle phase is calculated in the frame of the Flory−Huggins theory, the interfacial contribution being taken into account in terms of the Gibbs−Thomson model. The monomer activity in the aqueous phase is correlated by the NRTL equation. Model parameters were determined independently from the pressure−concentration data for the monomer−water and monomer−polymer binaries.

1. Introduction

Latex systems are produced by emulsion polymerization in water.[1] It is a colloidal dispersion of polymer particles in water. The polymerization of monomers rarely proceeds to completion, which leads to a certain level of unreacted monomer remaining in the polymer. The presence of residual monomers is undesirable, particularly when the monomers are toxic or when the residual volatile components might form an explosive mixture during transportation and/or storage. Contamination with unreacted monomers is especially a problem when the polymer is used for food packaging as well as in interior paints because the odor is particularly noticeable. Thus, removing the monomer rest from the resulting polymer product (i.e., latex) comes of essential value. To develop efficient process steps to remove the residual monomer or other volatile organic compounds (VOC), the partitioning of these substances between the aqueous and polymer-rich phases at low monomer content (up to saturation) is of particular importance.

Present work shows the experimental results on partitioning of vinyl acetate and butyl acrylate in two different latex systems at 65 °C. The data have been obtained using the static differential pressure method, which is detailed in section 2.

The thermodynamic modeling of partitioning of different volatile compounds in various latex systems has been reported by a number of authors.[2−14] Morton et al.[2] were the first to consider the monomer partitioning between the latex particles, monomer droplets, and the aqueous phase at swelling saturation. Balancing the Gibbs energy of mixing against the increase in surface energy due to equilibrium swelling, the authors derived a theoretical relation for the saturation swelling of latex particles. The Gibbs energy of mixing was described in the frame of the Flory−Huggins theory, and the interfacial Gibbs energy was expressed via the Gibbs−Thomson equation. Vanzo et al.,[3] Gardon,[4] and Maxwell et al.[5] extended the Morton equation to the unsaturated case (up to swelling saturation). Various authors[6,7,9] applied the model to describe the partitioning of two monomers. All the authors[2−14] normalized the monomer activity in the aqueous phase with respect to the reference state of the saturated monomer−water solution. Thus, at a given monomer concentration, the monomer activity in the aqueous phase was approximated by the ratio of the monomer partial pressure, P_M, to its partial pressure at saturation swelling, P_M^{LLV}. Assuming that the Henry law held for the polymer-free water phase up to the saturation point, Gardon[4] approximated this ratio, P_M/P_M^{LLV}, by the ratio of the aqueous-phase solubility of monomer below and at saturation as $[M]_M^W/[M]_M^{W,LLV}$, where $[M]_M^W$ and $[M]_M^{W,LLV}$ are the concentrations of monomer in the aqueous phase below and at saturation, respectively. Thus, to correlate partitioning, one needs the data on solubility of the monomer in water. The Flory−Huggins interaction parameter and the interfacial tension are to be obtained by adjusting to the experimental partitioning data for a given latex−monomer system (containing water, polymer, and monomer). No prediction based on the binary constituents (monomer−water and monomer−polymer systems) can be provided. Moreover, the reference state chosen to treat the monomer activity in the aqueous phase is not consistent with the Flory−Huggins lattice theory where the reference state is the pure liquid monomer.[15]

To overcome the inconsistency, in the present study, when thermodynamic equilibrium in a latex system is considered, it is proposed to calculate the monomer activities in both the polymer and aqueous phases starting from the reference state of a pure monomer. Appropriate activity coefficient models (or equation of state) can be used to express the Gibbs energy of mixing in the constituent binaries; e.g., the polymer-particle phase can be considered in terms of the Flory−Huggins

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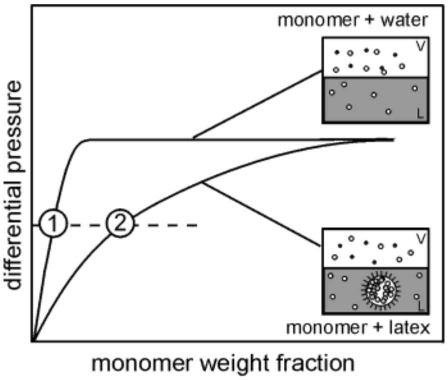


Figure 1. Basic idea of the measurements: Schematic differential pressure−weight fraction diagram; curve 1 is the system monomer−water, and curve 2 is the system monomer−latex.

or UNIFAC-FV model, while the NRTL or UNIFAC model can be applied to describe the aqueous phase. On this basis, the prediction of monomer partition coefficients is possible since no fitting to the experimental data on partitioning of the monomer between the equilibrium liquid phases for a given monomer−latex system is necessary. The activity coefficient model parameters can be found in databases or adjusted to the experimental pressure vs composition data in the corresponding monomer−water and monomer−polymer binaries.

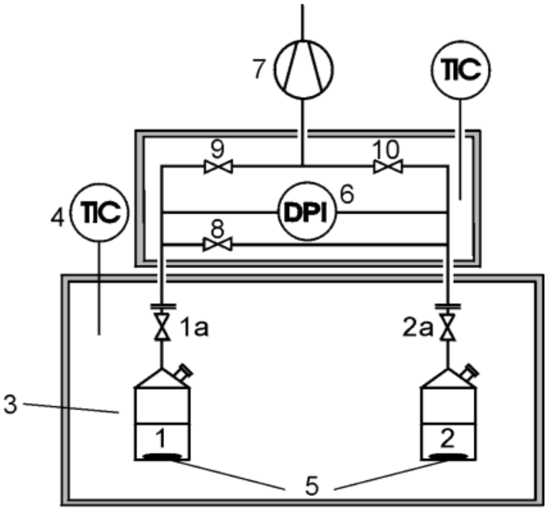
In the present study, the approach elaborated is utilized to represent the monomer partitioning in the latex systems studied experimentally. The Flory−Huggins model is used to describe the mixing Gibbs energy in the polymer-particle phase, the NRTL model is used to treat the aqueous phase. More details on the model are given in section 3. In section 4, the calculated results are compared to the experimental ones and to those calculated using the Vanzo approximation.[3]

2. Experimental Method

2.1. Experimental Procedure and Principle. The intention of the measurements is to obtain the partition of a monomer between water and polymer particles. Polymer is assumed to be practically insoluble in water, forming spherical aggregates (particles); water dissolves in the polymer particles also negligibly.[4] Thus, a "pure" latex system is considered as an emulsion of polymer particles in water. Monomer additives of interest are of limited solubility in water, whereas they are soluble in the polymer (at least within the concentration range under study). When such a monomer is present in the latex at concentrations below the saturation, it distributes between two liquid phases of the latex; only a limited amount of monomer is absorbed by the latex particles,[4] and the monomer concentration in the aqueous phase is restricted by its solubility in water.

Figure 1 shows schematically the principle of the procedure to determine the partition coefficients in latex systems at monomer concentrations up to saturation. To obtain the distribution coefficient, two sets of experimental data are to be considered. They are the concentration dependencies of differential pressure above the monomer−water system (curve 1, Figure 1) and that above the monomer−latex mixture (curve 2, Figure 1). A series of monomer injections to pure degassed water give curve 1; if the monomer is added to a degassed latex, curve 2 is attained. In both cases, at a fixed differential pressure, the monomer concentration in the aqueous phase is assumed to be of the same magnitude and thus can be defined from curve 1.

In the binary monomer−water system, the monomer is distributed between the liquid solution and the vapor phase. When the solubility of the monomer in water is reached, the differential pressure comes constant since a second liquid phase occurs. The monomer content in the liquid phase is estimated from the material balance; the vapor phase is assumed ideal.



1 reference cell with vent
2 equilibrium cell with vent
3 thermostat
4 PT 100
5 magnetic stirrer
6 pressure indicator
7 vacuum pump
8 bypass vent
9 reference side vent
10 equilibrium side vent

Figure 2. Differential pressure experimental setup.

If a certain amount of monomer is inserted into a vessel with latex, the monomer is distributed between all the phases present in the system: vapor and two liquid (polymer-particle and water-rich) phases. Under experimental conditions, the vapor phase is considered ideal. At a given differential pressure, the monomer amount in the aqueous phase is provided by its concentration in the aqueous phase which is obtained from the $P-x$ data for the binary monomer−water system (curve 1). The amount of the monomer in the polymer-particle phase, m_M^P, can be then estimated from the material balance equation as follows

$$m_M^P = m_M^L - m_M^W - m_M^V \qquad (1)$$

where m_M^L is the total mass of the monomer injected, m_M^W is the mass of the monomer in the aqueous phase (this value is taken from curve 1), and m_M^V is the mass of the monomer in the vapor phase.

The data can be converted to volume fractions using the component densities, the mixture specific volume being assumed the weighted average of the specific volumes of pure constituents. The distribution coefficient K is evaluated as a ratio of the monomer volume fractions in the polymer-rich (ϕ_M^P) and water-rich phases (ϕ_M^W) as follows:

$$K = \frac{\phi_M^P}{\phi_M^W} \qquad (2)$$

2.2. Experimental Setup. A static VLE apparatus (Figure 2) was designed for measurements of the solubility of a pure monomer in water and in a latex. The apparatus consists of two glass cells (reference cell (1) and equilibrium cell (2)), each

Table 1. Physicochemical Characteristics of Vinyl Acetate, Butyl Acrylate, and Latexes under Study at 65 °C

	VAc	BuA	latex VAc/BuA/AA	latex BuA/Sty/AA
copolymer ratio, wt %			67/31/2^{a}	78.5/18.5/3^{a}
molecular mass, g/mol	86.09^{b}	128.17^{b}	100000^{a}	100000^{a}
density, g/mol	0.87^{b}	0.85^{b}	1.13^{a}	1.03^{a}
particle radius, nm			66.25^{a}	79.70^{a}
Flory−Huggins binary interaction parameter χ			0.28^{c}	0.35^{d}
surface tension σ, N/m			$4 \times 10^{-5\ d}$	$4 \times 10^{-5\ d}$
saturation vapor pressure, mbar	777.95^{b}	57.55^{b}		
solubility in water in weight fractions	0.028 (60 °C)^{e}	0.0018^{f}		

[a] Reference 23. [b] Reference 22. [c] This work. [d] Reference 14. [e] Reference 3. [f] DECHEMA database.

being connected with a differential pressure indicator (DPI (6)). The DPI has an accuracy of 0.5% of a measured value. The cells have a capacity of about 60−80 mL (the volume of the static cells can be determined by using a gas solubility apparatus) and are submerged in a 70 L thermostat (3). Temperature is measured using resistance thermometers (PT 100 (4)) with an accuracy of 0.05 K.

For each experiment, water or latex is degassed in a separate apparatus. The amount of liquid in each cell is determined by weighing (accuracy of 0.1 mg). At the beginning of an experiment, both cells are filled up with the degassed water (in the monomer−water system measurement) or latex (when the latex-containing systems are under study) and connected with the DPI. The whole system is evacuated, and the bypass vent (8) is opened to equilibrate the pressure of the system and then closed again; the valves to the cells (1a, 2a) are opened. A small amount of a degassed monomer is injected through a septum into the equilibrium cell using a gastight syringe; the liquids in the cells are carefully agitated by a magnetic stirrer (5). The amount of monomer inserted is determined by weighing the syringe before and after injection with an accuracy of 0.1 mg.

Monomer concentration is gradually increased by injection of a known amount of monomer into the equilibrium cell to cover the desired composition range. The differential pressure is measured after each injection. Thus, the data on differential pressure as a function of monomer concentration in water or latex are obtained.

2.3. Chemicals. The monomer partitioning in two different latex systems was investigated. The latexes are vinyl acetate/butyl acrylate/acrylic acid (VAc/BuA/AA) with the copolymer weight composition of 78.5/18.5/3 and butyl acrylate/styrene/acrylic acid (BuA/St/AA) with the copolymer weight composition of 67/31/2. The latexes were provided by Elf Atochem, both purified by dialyzes in order to remove the excess surfactants, initiator, and residual monomers and thus to prevent polymerization. The solid content (the mass fraction of polymer particles in a "pure" latex) of the (VAc/BuA/AA) latex was 43 wt %. The (BuA/St/AA) latex was diluted with deionized water to give different solid contents about 50 to ca. 1 wt %. The monomers, vinyl acetate and butyl acrylate, were supplied by Sigma Aldrich and had a minimum purity of 99%. Water was deionized and degassed for the phase equilibria measurements in the monomer−water systems. The characteristics of the latexes and pure monomers used in this study are summarized in Table 1.

3. Modeling

Partitioning of a monomer in a latex has been described with a model similar to that of Vanzo.[3] It is based on considering the equilibrium between phases present in the latex−monomer system: polymer-particle and water-rich phases. In equilibrium the activities of monomer in both phases are equal:

$$a_{\mathrm{M}}^{\mathrm{W}} = a_{\mathrm{M}}^{\mathrm{P}} \tag{3}$$

Here $a_{\mathrm{M}}^{\mathrm{W}}$ is the monomer activity in the aqueous phase, and $a_{\mathrm{M}}^{\mathrm{P}}$ is the monomer activity in the polymer-particle phase.

The activity of the monomer in the polymer-particle phase is given by two terms:[3]

$$\ln a_{\mathrm{M}}^{\mathrm{P}} = \ln a_{\mathrm{M}}^{\mathrm{FH}} + \ln a_{\mathrm{M}}^{\mathrm{GT}} \tag{4}$$

The first term $a_{\mathrm{M}}^{\mathrm{FH}}$ characterizes polymer−monomer mixing, and it is calculated in the frame of the Flory−Huggins theory[16] accounting for both the combinatorial (entropic) and residual (enthalpic) contributions

$$\ln a_M^{FH} = \underbrace{\ln(1-\phi_P) + \left(1-\frac{1}{DP}\right)\phi_P}_{\text{entropic part}} + \underbrace{\chi\phi_P^2}_{\text{enthalpic part}} \tag{5}$$

where ϕ_{P} is the volume fraction of polymer in the polymer-particle phase, DP is the number-average degree of polymerization, and χ is the Flory−Huggins interaction parameter.

In addition, the interfacial contribution $a_{\mathrm{M}}^{\mathrm{GT}}$ is taken into account in terms of the Gibbs−Thomson equation[17]

$$\ln a_{\mathrm{M}}^{\mathrm{GT}} = \frac{2\sigma v_{\mathrm{M}}}{rRT} \tag{6}$$

where σ is the interfacial tension on the polymer particle/water interface, v_{M} is the molar volume of the monomer, and r is the radius of the swollen particle. Change in the particle radius on swelling has been introduced as[18]

$$r = \frac{r_{\mathrm{nonswollen}}}{\phi_{\mathrm{P}}^{\;1/3}} \tag{7}$$

The monomer activity in the aqueous phase is referred to a reference state of pure components and is described via activity coefficient ($a_{\mathrm{M}}^{\mathrm{W}} = x_{\mathrm{M}}^{\mathrm{W}}\gamma_{\mathrm{M}}^{\mathrm{W}}$), the latter being estimated from an appropriate activity coefficient model. In the present study, the NRTL equation (known to give reliable results for strongly nonideal mixtures with liquid−liquid demixing[19]) has been applied to represent the activity coefficients

$$\ln \gamma_i = \frac{\sum_{j=1}^{N}\tau_{ji}x_jG_{ji}}{\sum_{k=1}^{N}x_kG_{ki}} + \sum_{j=1}^{N}\frac{x_jG_{ij}}{\sum_{k=1}^{N}x_kG_{kj}}\left(\tau_{ij} - \frac{\sum_{m=1}^{N}\tau_{mj}x_mG_{mj}}{\sum_{k=1}^{N}x_kG_{kj}}\right) \tag{8}$$

where $\tau_{ij} = \Delta g_{ij}/RT$, $\tau_{ii} = 0$, $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $G_{ii} = 1$, Δg_{ij} is the interaction parameter in kelvin, α_{ij} is the

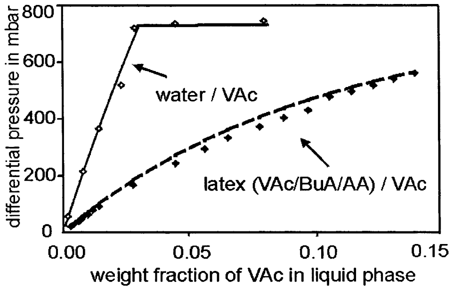


Figure 3. Differential pressure vs the liquid-phase concentration of vinyl acetate in its mixtures with water (◇) and with the (VAc/BuA/AA) latex (◆) at 65 °C; lines are the results of modeling: (—) the NRTL model, (- - -) this work.

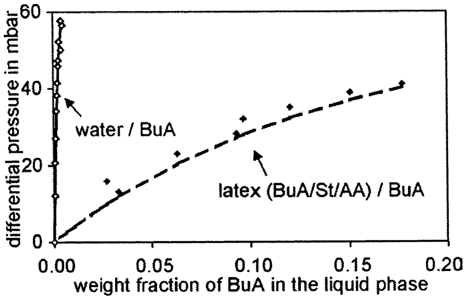


Figure 4. Differential pressure vs the liquid-phase concentration of butyl acrylate in its mixtures with water (◇) and with the (BuA/St/AA) latex (◆) at 65 °C; lines are the results of modeling: (—) the NRTL model, (- - -) this work.

Table 2. NRTL Parameters of the Vinyl Acetate−Water and Butyl Acrylate−Water Systems at 65 °C

parameter	vinyl acetate−water	butyl acrylate−water
Δg_{12}, K	1166	−812
Δg_{21}, K	1320	4423
α_{12}	0.3	0.3

nonrandomness parameter ($\alpha_{ij} = \alpha_{ji}$), and subscripts i, j, k, m specify one of N components of the aqueous phase.

4. Results and Discussion

Differential pressure in dependence on monomer content was measured in the solutions of vinyl acetate (VAc) and butyl acrylate (BuA) in water and the latexes based mainly on the corresponding monomers (Table 1). The measurements were carried out at 65 °C following the experimental procedure described in section 2. The differential pressure vs the weight fraction of VAc in the liquid phase in both water and the (VAc/BuA/AA) latex is plotted in Figure 3. The experimental data for BuA in water and in the (BuA/St/AA) latex are shown in Figure 4. Open rhombi belong to the data in the monomer−water systems and closed ones belong to those in the monomer−latex mixtures. The solubility of BuA in water was found to be 0.18 wt %, which is much lower than the solubility of VAc in water (2.9 wt %). The solubility data obtained are in an agreement with the values from the literature (see Table 1).

The upper solid lines in Figures 3 and 4 represent the results of fitting the experimental data on total pressure in the binary monomer−water systems using the NRTL model. The NRTL parameters estimated for the vinyl acetate−water and butyl acrylate−water binaries are summarized in Table 2. Parameters Δg_{12} and Δg_{21} were fitted to the experimental $P-x$ data for the monomer−water system by the least-squares method; α_{ij} was kept constant.

The dashed lines in Figures 3 and 4 relate to the results of calculation using the approach discussed in section 3. The results of modeling appeared to be in a good agreement with the data measured.

To perform the calculation, eq 3 and the material balance equation (monomer partitions between two liquid phases of the latex) were solved by iteration at each feed given; the monomer activities in the polymer and aqueous phases were calculated via eqs 4−7 using the corresponding parameters for the binary constituents. The NRTL parameters from Table 2 were used to calculate the monomer activities in the aqueous phase.

Parameters necessary to compute the monomer activity in the polymer-particle phase are given in Table 1. To receive the value of the Flory−Huggins interaction parameter (χ) for the vinyl acetate−polymer (VAc/BuA/AA) system, the VLE measurements were carried out utilizing the absorption apparatus described elsewhere.[20,21] The polymer was obtained by careful drying of the latex. The Flory−Huggins interaction parameter was considered composition independent, and its value was obtained by adjusting to the pressure−composition data in the VAc−polymer system. The Flory−Huggins interaction parameter for the butyl acrylate−polymer (BuA/St/AA) system was taken from Gugliotta et al.[14] For both latex systems, the values of surface tension reported in Gugliotta et al.[14] were accepted in the calculations. The diameter of the unswollen polymer particles were provided by the Universidad del País Vasco[23] as measured using the dynamic light scattering technique.

To illustrate the ability of the model to predict the pressure in monomer−latex systems, Figure 5 summarizes the data on the total pressure above the butyl acrylate−(BuA/St/AA) system for the latexes of different solid content. The solid content varies between 0.8 and 50 wt %. As seen from the figure, the model (lines) reproduces well the pressure changes with composition obtained experimentally (points) for all solid contents examined.

The effect of different factors on the monomer partitioning can be made by analyzing the contributions to the monomer activity in the polymer-particle phase. In Figure 6, the three activity terms are depicted as a function of the polymer volume fraction in the polymer-particle phase on the example of the VAc−latex system. As seen from the figure, the entropic part has the dominant impact whereas the enthalpic as well as the interfacial contributions are much less valuable. The calculation results were found affected to some extent by the value of the χ parameter (considered here as composition independent). Depending on the χ value, the activity curve shifts somewhat up or down (taking into account the composition dependence could slightly change the slope of the curve), the best results being obtained when the parameter value corresponds to that adjusted to the experimental data on VLE in the binary VAc−polymer system. It is apparent that the differing in particle sizes has a small effect on the monomer partitioning,[5] and as a fact the corresponding interfacial term contributes to the activity insignificantly.

On the basis of the activity data (experimental and calculated), the compositions of both the polymer-particle and aqueous phases were evaluated. The results are demonstrated in Figures 7 and 8, where the monomer weight fraction in the latex-particle phase is plotted vs the monomer weight fraction in the aqueous phase.

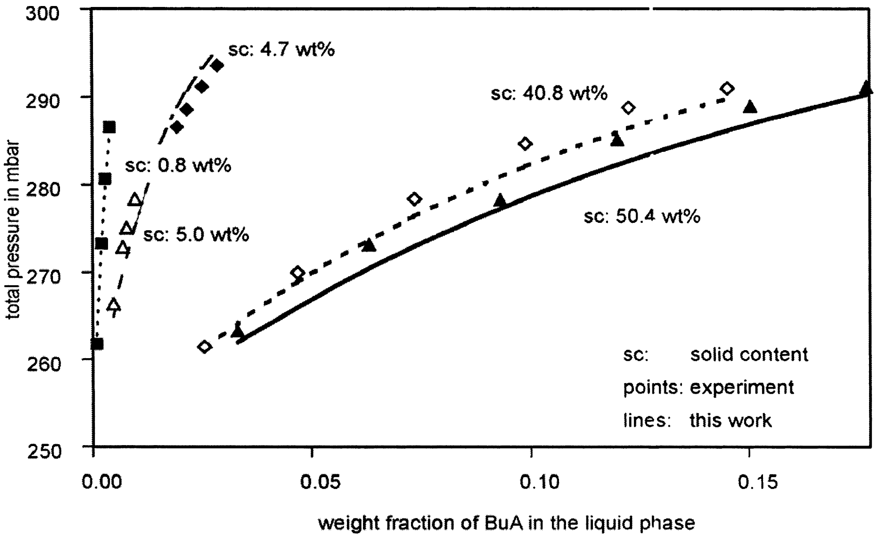


Figure 5. Comparison of experimental and calculated values of total pressure at 65 °C in the mixtures of butyl acrylate with the (BuA/St/AA) latex of different solid contents (sc): (■,- - -) 0.8 wt %; (◆, — —) 4.7 wt %; (△, - • -) 5.0 wt %; (◇,- - -) 40.8 wt %; (▲, —) 50.4 wt %.

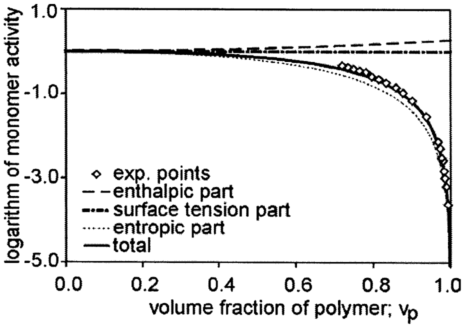


Figure 6. Composition dependence of the activity of vinyl acetate in the polymer-particle phase for the VAc–(VAc/BuA/AA) latex system at 65 °C.

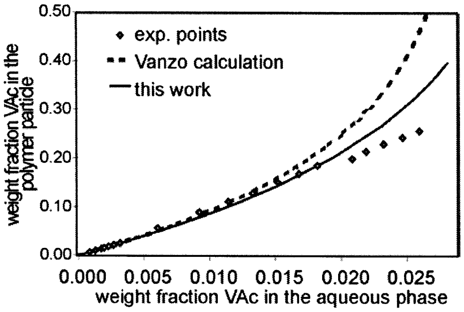


Figure 7. Weight fraction of vinyl acetate in the (VAc/BuA/AA) latex particles as a function of its weight fraction in the aqueous phase at 65 °C.

The experimental points are depicted by diamonds. The solid lines indicate the results of modeling with the help of the approach proposed in the present study (see section 3). The modeling outcomes are in a good agreement with the experimental data. For comparison, the dashed lines show the results of calculation using the Vanzo approximation, where the saturated monomer–water solution is chosen as a reference state to treat the aqueous phase. As seen, the deviation of the dashed lines from the experimental points (as well as from the values calculated within the model elaborated) increases with growing the monomer concentration in the aqueous phase. In both systems, analogous behavior is observed.

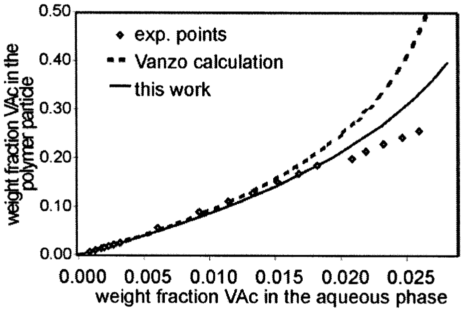


Figure 8. Weight fraction of butyl acrylate in the (BuA/St/AA) latex particles as a function of its weight fraction in the aqueous phase at 65 °C.

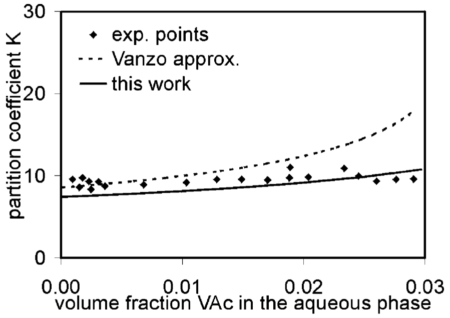


Figure 9. Partitioning of vinyl acetate between the polymer-particle and aqueous phases at 65 °C.

The partition coefficients of VAc and BuA in the corresponding latexes were evaluated as a function of composition. Rhombi in Figures 9 and 10 represent the experimental partition coefficients of VAc in the (VAc/Sty/AA) latex and BuA in the (BuA/Sty/AA) latex, respectively. From the values of partition coefficient obtained, it is recognizable that the concentration of vinyl acetate in the polymer-particle phase is approximately 10 times higher than in the aqueous phase. The solubility of BuA in water is very low; as a result, its partition coefficient in the corresponding latex is extremely high. The concentration of BuA in the polymer particles exceeds the BuA content in the aqueous phase ca. 140 times. In this system, the partition coefficient values are much greater than ones in the case of the VAc–latex system.

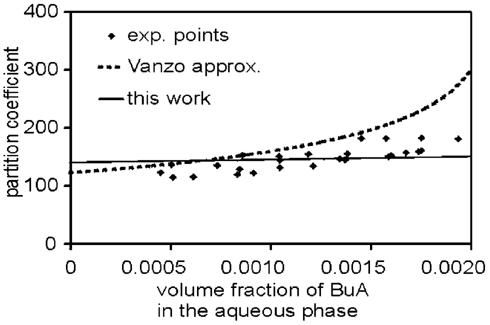


Figure 10. Partitioning of butyl acrylate between the polymer-particle and aqueous phases at 65 °C.

Lines in Figures 9 and 10 relate to the modeling results. In contrast to the values calculated using the Vanzo approximation (dashed lines), partition coefficients calculated in terms of the approach proposed here (solid lines) are in a good conformity with the experimental results. The discrepancy between experimental points and the Vanzo model increases with rising the monomer content in the aqueous phase. The consistent choice of the reference state for the aqueous phase makes it possible to describe the partition coefficients within the composition range up to saturation in a better way, whereas the Vanzo approximation overestimates the partition coefficient values at higher monomer (close to saturation) concentrations.

5. Conclusions

A static differential pressure technique has developed to determine the partitioning of monomers between the aqueous and polymer-rich phases in latex systems. Partition coefficients as a function of monomer concentration have been measured for the vinyl acetate−(VAc/BuA/AA) and butyl acrylate−(VAc/Sty/AA) systems at 65 °C.

A modification of the thermodynamic model developed by Vanzo[3] is used to represent the experimental data. The model is based on the Flory−Huggins theory and the Gibbs−Thomson equation to estimate the monomer activity in the polymer-particle phase, while the NRTL equation is applied to model the monomer activity in the aqueous phase. The data needed for the calculation are the binary VLLE parameters for the monomer−water system (e.g., NRTL parameters), the Flory−Huggins interaction parameter χ for the binary monomer−polymer system, and the interfacial tension between the polymer-particle and aqueous phases as well as the particle radius in the pure latex system. The modification proposed has been utilized to correlate the partition coefficients in the latex systems under study. The results are in a good agreement with the data measured.

The model can be easily extended to calculate the partitioning of two or more monomers between the polymer and water phases in a variety of latexes.

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