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ORIGINAL CONTRIBUTION

K. Tauer
H. Kaspar
M. Antonietti

Equilibrium swelling of colloidal polymeric particles with water-insoluble organic solvents

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K. Tauer (✉) · M. Antonietti
Max Planck Institute of Colloids
and Interfaces
Am Mühlenberg, 14476 Golm, Germany
e-mail: klaus.tauer@mpikg-golm.mpg.de
Tel: +49-331-5679511
Fax: +49-331-5679512

H. Kaspar
Dyneon GmbH, Werk Gendorf
84504 Burgkirchen, Germany

Abstract The Morton–Kaizerman–Altier (MKA) equation fails to describe experimental swelling data of polystyrene particles with toluene in the absence of free or adsorbed surfactants. A modification of the MKA equation is possible by the consideration of a volume work leading to a swelling pressure in analogy to macroscopic gels. With the modified equation a satisfactory description of the experimental data is possible if a size dependence of all the three interaction parameter of the particles with the swelling agent, the swelling pressure, and the interfacial tension of the particles is considered. In the case of particles with diameters below 50 nm and with high surface charge densities an additional electrostatic repulsion contributes to the volume increase during swelling, which is not yet considered in the theory.

Key words Latex particles · Swelling · Interfacial tension · Swelling pressure · Size dependence

Introduction

It is generally accepted that the main locus of monomer consumption during the emulsion polymerization of water-insoluble monomers is the monomer swollen latex particle phase. Thus, the monomer concentration inside the particles is of considerable interest for the optimization of as well as for controlling the polymerization process. Furthermore, the ability of controlling the swelling process can be exploited to tailor polymeric particles by swelling for different applications, including subsequent polymerization or the use as containers for various valuable goods.

It is the state of the art [1, 2] to consider latex particle swelling, at least theoretically according to an equation published in 1954 by Morton, Kaizerman, and Altier (MKA) [3] although problems with its practical application are known [4–8].

In a previous publication the attempt was made to explain the deviation of the experimental swelling data from the MKA equation in a more theoretical way by considering an additional osmotic pressure term and a size-dependent depletion correction [8]. Although this ansatz significantly improved the data interpretation, there were still systematic deviations, suggesting the incompleteness of the description. The aim of this contribution is twofold. Firstly, the swelling of latex particles is considered in a more pragmatic way than in the previous publication [8] in analogy to the swelling of macroscopic gels. Thus, besides the surface work a volume work is introduced in the MKA equation, also leading to the consideration of a swelling pressure. Secondly, the size dependence of the swelling capacity is considered in more detail and relations are introduced describing the size dependence of the interfacial tension, the particle–swelling agent interaction parameter, and the swelling pressure in a semiempirical way.

This article is organized in such a way that after some general remarks on swelling an attempt is made to use the MKA equation to describe previously published experimental results [8] obtained with model latexes. As this failed, stepwise modifications of the MKA equation are made, leading to a satisfactory fit of the experimental data sets, thus underlining the importance of both the swelling pressure and the particle-size-dependent corrections. The terms solvent, swelling agent, and monomer are used in the following interchangeably.

Experimental

The synthesis of the model latexes as well as their characterization and the carrying out of the swelling investigation were described in detail elsewhere [8].

Swelling – general remarks

Most of the monomers (styrene, acrylates, and methacrylates) are good solvents for their own and other polymers; however, just as other organic solvents they are not able to dissolve the colloidal polymer particles of an aqueous dispersion. The particles imbibe only a limited amount of solvent even if it is present in the form of a bulky free phase. This behavior resembles the behavior of macroscopic gels, which also absorb less solvent than the amount corresponding to the equilibrium condition $\Delta\mu_1 = 0$, where μ_1 is the chemical potential of the solvent. To achieve thermodynamic equilibrium under these circumstances, an additional contribution – the swelling pressure – has to be considered. The swelling pressure prevents the gel from being swollen to its maximum and is identical with the osmotic pressure of a polymer solution, assuming the gel itself forms the semipermeable membrane [9, 10]. Consequently, the same relation as in the case of the osmotic pressure holds (Eq. 1).

$$\Delta\mu_1 = -\pi_s v_1 \ , \tag{1}$$

where π_s is the swelling pressure and v_1 is the molar volume of the solvent.

The MKA equation

MKA assumed according to Eq. (2) that only the partial molar free interfacial energy prevents the particles from dissolving, i.e. from maximum swelling.

$$\Delta\mu_1 = -\frac{2\gamma v_1}{r} \ , \tag{2}$$

where γ is the interfacial tension between the particle and the dispersion medium and r is the swollen particle radius. In other words, Eq. (2) contributes to the fact that the chemical potential of a particular component in a mixed phase depends on the molal interfacial area of that phase.

Equation (3) results if for the change in the chemical potential of the solvent the Flory–Huggins–Rehner expression for cross-linked polymers is used.

$$\left(\frac{2\gamma}{r}\right)\frac{v_1}{RT} = -\left[\ln(1-\phi_2) + (1-1/j_2)\phi_2 + \chi\phi_2^2 + \frac{v_1\rho_2}{\bar{M}_C}\left(\phi_2^{1/3} - \phi_2/2\right)\right] \ , \tag{3}$$

where χ is the polymer solvent interaction parameter, ϕ_2 is the polymer volume fraction in the swollen particle, RT is the thermal energy, j_2 is the average degree of polymerization of the polymer molecules, ρ_2 is the polymer density, and $\bar{M}_C$ is the average molecular weight between two cross-links in the network. If the latex particle is not cross-linked ($\bar{M}_C \Rightarrow \infty$) Eq. (3) is identical to the MKA equation as derived by Gardon [11]. The relation $\phi_1 + \phi_2 = 1$ exists between ϕ_1, the monomer volume fraction, and ϕ_2. The swollen and unswollen particle radii (r_0) are connected to ϕ_2 via $(r/r_0)^3 = 1/\phi_2$.

The failure of the MKA equation

Equation (3) predicts that the swelling capacity of latex particles depends on the interfacial tension between the particles and the continuous phase, the particle size, the molecular weight of the polymer, the Flory–Huggins interaction parameter between the polymer and the swelling agent, and the cross-linking density of the particles.

Contradictory results are known concerning the use of the MKA equation to calculate the equilibrium swelling of latex particles [4–8]; however, MKA [3] were able to show the applicability of Eq. (3) for equilibrium swelling data. With Eq. (3) they obtained from equilibrium swelling data for uncross-linked high-molecular-weight polystyrene latex particles and toluene as a swelling agent ($j_2 \Rightarrow \infty$ and $\bar{M}_C \Rightarrow \infty$) at 25 °C reasonable values for γ and χ: 3.5 mN m^{-1} and 0.48, respectively. For styrene as a swelling agent the authors obtained $\chi = 0.43$ and $\gamma = 4.5$ mN m^{-1}. In contrast, Gardon [11] determined $\chi = 0.35$ and $\gamma = 35$ mN m^{-1} polystyrene/styrene system at 25 °C. For the same system at 30 and 60 °C Vanzo et al. [12] obtained $\chi = 0.30$, $\gamma = 31.2$ mN m^{-1} and $\chi = 0.26$ and $\gamma = 12.4$ mN m^{-1}, respectively. Note, for both χ and γ quite different values are obtained with these three sets of experimental data; however, the most remarkable difference between the data is with respect to the values of the interfacial tension. Values of the order of 30 mN m^{-1} are quite high as for pure polystyrene the interfacial tension to pure water is 32.7 mN m^{-1} [13]. In connection with this it is necessary to point out that all these latex particles were stabilized by surfactants to impart stability during the swelling experiments. The value of γ determined in swelling experiments should be much lower than 32.7 mN m^{-1} as besides the surfactants the dissolved swelling agent in water also leads to a reduction in the interfacial tension. In the latter two cases sodium dodecyl sulfate at concentrations below the critical micelle concentration was used. On the other hand, MKA [3] had stabilized the latexes with such an amount of potassium laurate that at the swelling equilibrium the particle surface was completely covered and, hence, surfactant micelles were present. The authors noticed that under these circumstances the latexes imbibed more than twice as much swelling agent compared to the case without added soap, but for the evaluation they used the data sets obtained in the presence of soap. From this brief review it becomes obvious that surfactants have a strong influence on the result of swelling experiments. Surfactant micelles can imbibe swelling agent and adsorbed surfactant layers can incorporate swelling agent due to adsolubilization, but molecularly dissolved surfactant molecules can also cause an increase in the water solubility of the swelling agent [14].

To avoid the presence of surfactants, but to ensure the latex stability, swelling experiments were carried out with carefully cleaned polystyrene latexes prepared in the presence of reactive surfactants and functional comonomers, respectively, as described previously [8]. These experiments are unique so far as the latexes contain absolutely no free or adsorbed surfactants. Moreover, the surface of the latex particles is well characterized and consists of either sulfonate groups with varying charge densities (σ) (sulfonate latexes) or nonionic gluconosiloxane moieties (sugar latex). Also a loosely cross-linked latex [molar ratio of styrene to 1,3-di(isopropylene)benzene of 150] containing hydroxyl surface groups as well as very few sulfate groups (hydroxyl latex) was included in the investigations. Figure 1 compares these experimental data on latex swelling with calculations according to Eq. (3) by means of changes in ϕ_1 with the diameter of the swollen particles (D). The experimental data confirm two predictions of the MKA equation: the dependence of ϕ_1 on both the particle size and the interfacial tension. Furthermore the results depicted in Fig. 1 corroborate the importance of free or adsorbed surfactants on the swelling of colloidal particles. The experimental data as well as the calculations show that the swelling is greater the lower the interfacial tension. Particles with a higher surface charge density swell more than particles of the same size but with a lower surface charge density. This is a first approximation to explain within the assumption that a higher σ means a lower γ and vice versa. Theoretical curves can be nicely fitted to the experimental data with different values of the interfacial tension. For the MKA data a γ value of 4 mN m^{-1} fits the data almost perfectly. On the other hand, the γ values needed to fit the experimental ϕ_1 data for the purified sulfonate and hydroxyl or sugar latexes are 30 and 100 mN m^{-1}, respectively. These values are unreasonably high as one would expect γ, at least for the sulfonate latexes, to be of the order of 10 mN m^{-1} and in any case clearly below 32.7 mN m^{-1}. A γ value of about 4 mN m^{-1} to fit the swelling data when both a saturated potassium laurate layer at the particle interface and potassium laurate micelles are present is reasonable. This is almost the same value as for the toluene–water interface saturated with potassium laurate which was measured with the drop–volume method to be about 4 mN m^{-1} [15].

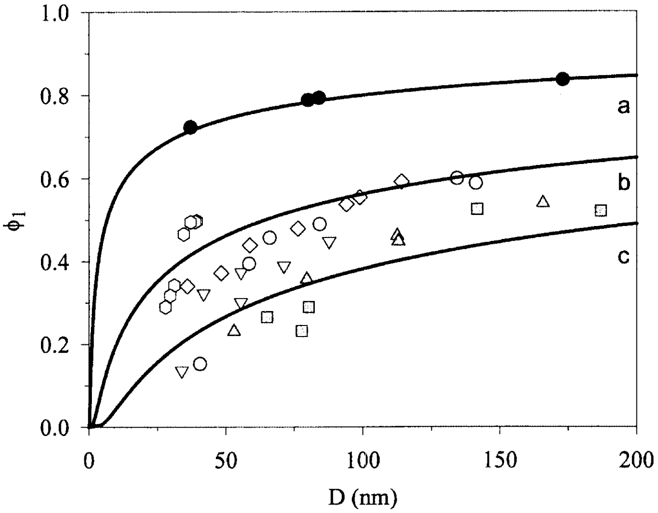

Fig. 1 Dependence of experimental values of ϕ_1 on the particle size for polystyrene latexes with different surface decorations (*points*) and model calculations using Eq. (3); swelling agent toluene. Data from Morton, Kaizerman, Altier [3] (●); sulfonate latex 1, $\sigma = -19$ μC cm^{-2} (⬡); sulfonate latex 2, $\sigma = -8.6$ μC cm^{-2} (◇); sulfonate latex 3, $\sigma = -7.5$ μC cm^{-2} (○); sulfonate latex 4, $\sigma = -4$ μC cm^{-2} (▽); sugar latex (△); hydroxyl latex (▨). σ is the surface charge density of the cleaned latexes determined by titration with hyamine in a Mütek PCD 02 charge detector before fractionation in a preparative ultracentrifuge as described in Ref. [8]. The calculations were carried out with $v_1 = 9.36$ mmol cm^{-3}, $T = 298.15$ K, $c = 0.45$, $j_2 \Rightarrow \infty$, $\bar{M}_C \Rightarrow \infty$, curve *a*: $\gamma = 3$ mN m^{-1}, curve *b*: $\gamma = 30$ mN m^{-1}, curve *c*: $\gamma = 100$ mN m^{-1}

These results show that the MKA equation fails to describe the swelling behavior of neat polymeric particles as with reasonable γ values it predicts too high ϕ_1 values, but it is obviously suited to describe the swelling behavior of systems containing micelles. This leads to the conclusion that the MKA equation does not take into account all specific contributions caused by the polymeric nature of the latex particles.

The consideration of a volume work

Polymeric latex particles behave significantly differently during the interaction with solvents than micelles or oil droplets of a similar size. Obviously, an additional resistance to swelling besides the contribution of the interfacial free energy has to be taken into account.

This additional resistance may originate from a volume work due to attractive forces between the

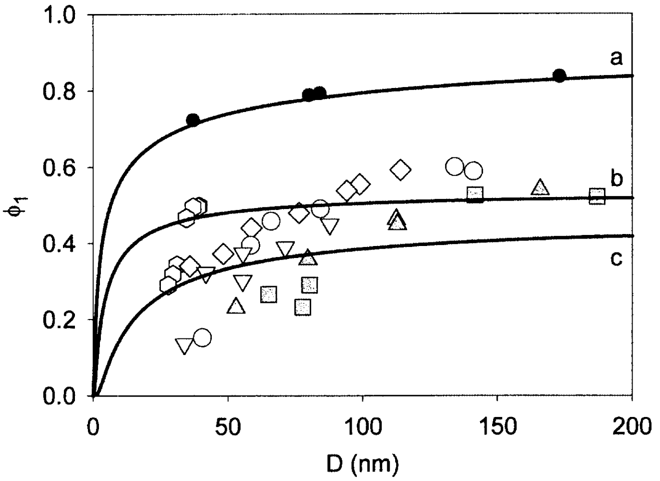

Fig. 2 Impact of the swelling pressure on calculated ϕ_1–D curves according to Eq. (4). For the meaning of the symbols (experimental values) see caption of Fig. 1. The calculations were carried out with $v_1 = 9.36$ mmol cm^{-3}, $T = 298.15$ K, $c = 0.45$, $j_2 \Rightarrow \infty$, $\bar{M}_C \Rightarrow \infty$, curve a: $\gamma = 3$ mN m^{-1} and $P = 10^4$ N m^{-2}, curve b: $\gamma = 8$ mN m^{-1} and $P = 1.5 \times 10^6$ N m^{-2}, curve c: $\gamma = 36$ mN m^{-1} and $P = 2.5 \times 10^6$ N m^{-2}

polymer chains. Note, the existence of attractive forces between chains in concentrated polymer solutions has been concluded from osmotic modulus measurements [16]. An equilibrium swollen latex particle represents a highly concentrated polymer solution of about 1 g cm^{-3}. The consideration of a volume work ($P\,\mathrm{d}V$, where P is the pressure and $\mathrm{d}V$ the volume change during swelling) leads to Eq. (4).[1]

$$\left(\frac{2\gamma}{r} + P\right)\frac{v_1}{RT} = -\left[\ln(1 - \phi_2) + (1 - 1/j_2)\phi_2 + \chi\phi_2^2 + \frac{v_1\rho_2}{\bar{M}_C}\left(\phi_2^{1/3} - \phi_2/2\right)\right] \tag{4}$$

The pressure in Eq. (4) can be considered as the swelling pressure of colloidal particles contributing together with the partial molar free interfacial energy to the equilibrium in the chemical potential of the swelling agent. It is of the order of up to some hundred bars, depending on the decoration of the particle interface [8]. The impact of P on the calculated ϕ_1–D curves according to Eq. (4) is illustrated in Fig. 2. The theoretical curves are now shifted into the region of the experimental data points with much lower γ values compared to the plots in Fig. 1. These values are 8 and 36 mN m^{-1} for the sulfate and the uncharged latexes, respectively.

By rewriting Eq. (4) in the more lucid form of Eq. (5) the similarity between latex particle swelling (the uptake of solvent molecules by a polymer particle) and the reverse process, namely the stabilization of emulsion droplets by trapped species which are insoluble in the continuous medium (for instance the uptake of polymer molecules by a solvent droplet) as described in Ref. [17], becomes obvious.

$$\Delta\mu_1 = \left[\frac{2\gamma}{r} + P\right]v_1 \tag{5}$$

Note, Eq. (5) is, despite a factor in the γ term, basically similar to Eq. (4) in Ref. [8]. The limiting cases of the modified MKA equation with respect to $r \Rightarrow \infty$ and $\phi_2 \Rightarrow 0$ are of special interest. In the case of a bulk polymer ($r \Rightarrow \infty$) the resulting equation is the osmotic or swelling pressure relation given by Eq. (1) with $P = -\pi_s$ [9]. If the polymer concentration is vanishing ($\phi_2 \Rightarrow 0$) the Young–Laplace equation for a colloidal droplet or bubble embedded in a fluid phase results [18]. This is an expression for the situation where the swollen latex particles represent a polymer gel or solution but with colloidal dimensions.

The size dependence of the swelling parameters

The data combined in Figs. 1 and 2 reveal that neither Eq. (3) nor Eq. (4) describes the measured size dependence correctly, especially if the particle diameter is below 100 nm. This leads to the conclusion that essential parameters in the swelling equation have to be considered to be dependent on the particle size. Particularly, these are the interfacial tension, the Flory–Huggins interaction parameter, and the swelling pressure.

The dependence of γ on the size of colloidal objects was introduced by Gibbs [19] and later developed theoretically on a thermodynamics basis for a one-component two-phase system by Tolman [20]. The basic idea is to define besides the surface of tension (a_s) a surface which makes the superficial density vanish (a_v). The difference in distance from the sphere center to both surfaces ($\delta = a_v - a_s$) is maximum in the magnitude of the thickness of the interfacial layer [21]. The numerical value of δ/r determines how great the size dependence of γ is, but the sign of δ/r determines whether γ decreases ($\delta > 0$) or increases ($\delta < 0$) [21]. Calculations based on statistical mechanics for liquid argon at 90 K [22] suggest that δ is positive and approximately 3 Å. This value leads to a 6% decrease (increase) in γ for a droplet (bubble) of 10-nm radius compared with a plane surface [21].

Another way to express the size dependence of the interfacial tension is given by Eq. (6), where γ_∞ denotes the interfacial tension of a plane surface and λ_1 is an empirical parameter accounting for the interfacial layer thickness.

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[1] The change in the free energy of the swelling agent is now counterbalanced by $\gamma\,\mathrm{d}A + P\,\mathrm{d}V$, which leads with $\mathrm{d}A = (2/r)\,\mathrm{d}V$ and $\mathrm{d}V = v_1\,\mathrm{d}n_1$ to Eq. (4), where $\mathrm{d}n_1$ is the number of moles of swelling agent needed for equilibrium swelling

$$\gamma(r) = \gamma_\infty \left(1 + \frac{2\lambda_1}{r}\right) \tag{6}$$

Equation (6) is very similar to an equation derived on the basis of the surface-free-energy equation for a generally curved interface as described in Ref. [23] when the r^{-2} term is neglected.

The size dependence of χ is expressed in a similar way, where the influence of the thickness of the chemically different interfacial layer is expressed by λ_2:

$$\chi(r, \phi_2) = \chi_\infty \left(1 + \frac{3\lambda_2}{r}\right) \tag{7}$$

The justification for this procedure is given by the fact that χ for a particular polymer solvent system is by no means constant. Besides, the influence of the chemical composition of the interfacial layer χ depends on ϕ_2, j_2, and the temperature [24]. The important one of these three parameters for the swelling experiments is ϕ_2 as the measurements were carried out isothermally and j_2 is so high that it has practically no influence. During the swelling experiments ϕ_2 changes from 1 to almost 0.4 and this alone causes an increase in χ. For the polystyrene–toluene bulk system a quantitative relation between χ and ϕ_2 was determined at 25 °C as given by Eq. (8) [25].

$$\chi_\infty(\phi_2) = 0.431 - 0.311\,\phi_2 - 0.036\,\phi_2^2 \tag{8}$$

Note, a ϕ_2 dependence of χ can be translated into a r dependence for swelling experiments as between both values there exists an indirect correlation (cf. experimental data in Figs. 1 and 2). Furthermore, a latex particle represents per se with respect to χ an inhomogeneous structure due to the different composition of the particle interior (more hydrophobic) compared with the particle interface (more hydrophilic). Hence, a χ value independent of the particle size is only a crude approximation, especially for particles smaller than 50 nm in diameter, as with decreasing r the overall particle properties are governed more and more by the properties of the interface.

Concerning the swelling pressure, a justification for introducing a dependence on the particle size originates from the swelling behavior of polystyrene microgels in toluene which was investigated by size measurements with dynamic light scattering [26, 27].[2] Using these data the swelling pressure can be calculated according to Eq. (4) by setting $\gamma = 0$. Although these values scatter, a distinct correlation, $P \propto r^{-1}$, is given (Fig. 3), which vanishes for bulk samples ($r \Rightarrow \infty$).[3] The relation given by Eq. (9) will be used in the further considerations; admittedly a factor (Z) is introduced by taking into account the transition from the quasihomogeneous microgel system in toluene to the heterogeneous aqueous systems of charged polystyrene in the presence of toluene.[4] The factor Z acts directly on P_0. P_0 represents the swelling pressure of chemically identical bulk materials and P^* can be considered as a modulus describing the pressure increase with decreasing size of the sample.

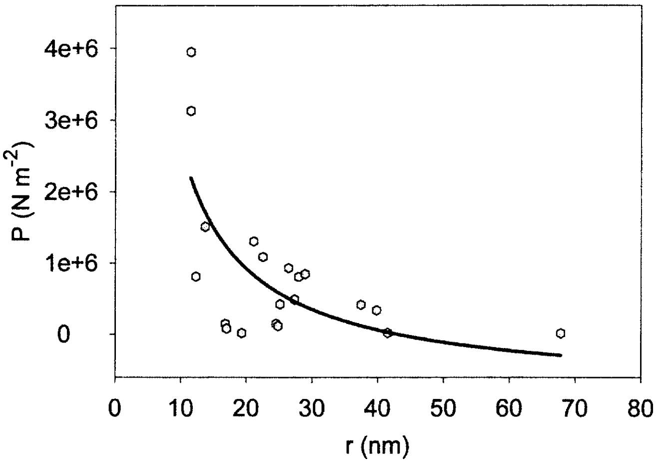

Fig. 3 Swelling pressure of polystyrene microgels in toluene according to Eq. (4) with $\gamma = 0$. The *points* represent experimental data [26, 27] and the *line* is the fit according to $P = P_0 + (P^*/r)$, with $P_0 = -8.018716 \times 10^5$ N m^{-2} and $P^* = 34.45$ mN m^{-1}

$$P = P_0 + \frac{P^*}{r} \tag{9}$$

Equations (6)–(9) were used to modify Eq. (4) with respect to γ, χ, and P and subsequently to fit the swelling data. The results depicted in Fig. 4 were obtained with a common set of numerical values for γ_∞, λ_1, P_0, P^*, and Z for all series of experimental data. The only parameter which it was necessary to change was λ_2 in Eq. (7). The λ_2 values for the sulfonate series (with the exception of the sulfonate series with the highest surface charge density) and for both the sugar and hydroxyl latexes are 17 and 43 nm, respectively. This seems to be a remarkable result for several reasons. Firstly, the swelling of latex particles is a volume effect and hence the particle–solvent interaction has a stronger influence than the interfacial tension.[5] Secondly, the chemical nature of the stabilizing groups has a strong influence on the thickness

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[2] The determination of the swelling capacity by size measurements is not the optimum method [8] as these measurements are not sensitive enough compared with volume methods, but other data are alas not available

[3] $P_0 = -8.018716 \times 10^5$ N m^{-2} and $P^* = 34.45$ mN m^{-1} in the correlation

[4] The factor Z is of the order of 10^{-4}

[5] Note that the continuous medium as well as the particles including the interfacial or stabilizer layer (it makes no difference if this is covalently bound or adsorbed) are saturated with the swelling agent and, hence, a constant and low value of γ for all systems, including the MKA data, is reasonable

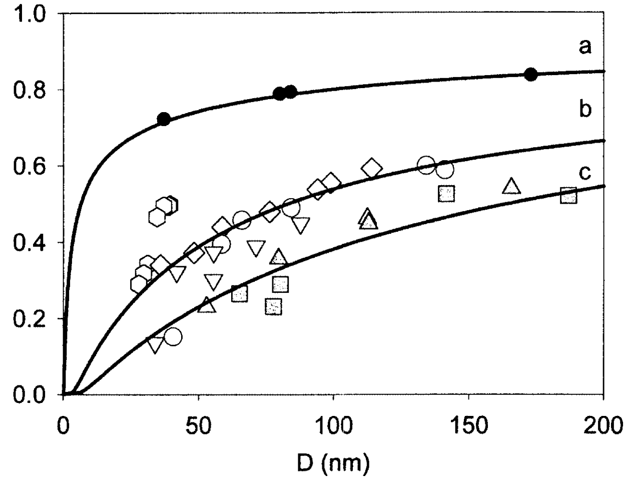

Fig. 4 Experimental ϕ_1 versus D relations (for the meaning of the symbols see the caption of Fig. 1) and calculated curves according to Eq. (4) (curve *a*) with size-dependent corrections for γ, χ, and P (curves *b*, *c*). Curve *a*: $\gamma = 3$ mN m^{-1} and $P = 10^4$ N m^{-2} (no size dependence), curves *b*, *c*: $\lambda_1 = 2$ nm; $\gamma_\infty = 4$ mN m^{-1}; $P_0 = -8.018716 \times 10^5$ N m^{-2}; $Z = 1 \times 10^{-4}$; $P^* = 34.45$ mN m^{-1}; $T = 298.15$ K; curve *b*: $\lambda_2 = 17$ nm; curve *c*: $\lambda_2 = 43$ nm

of the interfacial layer and, hence, on the value of λ_2. Thirdly, the fitted curves *b* and *c* show the clear tendency that for very small particles in the absence of surfactants the swelling ability almost vanishes. Fourthly, if low-molecular-weight stabilizers dominate the swelling behavior no size-dependent corrections are necessary.

These results lead to the conclusion that with respect to the monomer concentration inside the particles during emulsion polymerization systematic investigations in the presence of varying surfactant concentrations are necessary. Furthermore, the kinetically accessible monomer concentration inside the particles is influenced by the diffusion rate of the monomer into the particles in relation to the monomer consumption rate by polymerization [28]. This rate ratio can be influenced by both the kind and the concentration of the surfactant.

The behavior of the highly sulfonated latexes (sulfonate latex 1) appears to call for comment as the ϕ_1 size dependence obviously cannot be described with the common parameter set. Compared to the less charged sulfonate latexes the slope is much larger, indicating an apparently better swellability of the highly charged latexes. The failure of the common parameter set can be explained by the combination of the high sulfonate content and the small particle size, which makes these particles with respect to the interaction, different from all the other latexes (different Z, χ, and γ_∞). Furthermore, due to the uptake of the swelling agent the chain mobility inside the particles is increased and the charges can now arrange themselves as far as possible from each other, leading to a more stretched chain conformation. Hence, the apparently larger ϕ_1 $[(D/D_0)^3 = 1/(1 - \phi_1)]$ may not alone be caused by an increased swelling, but additionally also by expansion of the particles due to electrostatic repulsion. The contribution of electrostatic repulsion has not been considered in the theoretical treatment of latex particle swelling so far; however, the theory of the swelling behavior of charged macroscopic gels is well developed [29–31] and a corresponding treatment of latex particle swelling seems possible in the future.

Conclusion

To understand and subsequently to control latex particle swelling is one of the basic challenges in the field of polymer dispersions. The swelling of latex particles is not only governed by the change in the free interfacial energy and the solvent particle interaction. Moreover, the swelling of polymeric nanoparticles is additionally controlled by a swelling pressure as a result of a volume work which is done during swelling of the system.

To fit experimental swelling data of polystyrene latex particles with toluene in the absence of surfactants a size dependence of χ, P, and γ has to be considered. In the case of particles with diameters below 50 nm and with high surface density the electrostatic repulsion of the charged chain segments additionally contributes to the expansion of the particles.

Furthermore free, adsorbed, and micellar surfactants have a strong influence upon the swelling behavior. The influence of both charge repulsion and surfactants upon swelling of polymeric nanoparticles has not yet been incorporated in a general theoretical description.

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