

# Experiments and Thoughts on Mass Transfer During Emulsification



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*This paper is dedicated to Prof. Dr. H. U. Moritz on the occasion of his 65th birthday.*

**Abstract** The traditional way of making emulsions is via the input of extra mechanical energy, but there is another mechanism of emulsification that is entirely thermodynamically controlled. Experimental results are presented elucidating the consequences of this spontaneous emulsification for heterogeneous reaction systems. Special emphasis is placed on aqueous heterophase polymerization. We present the results of unusual experiments in oil–water systems that fundamentally changed our view of the mechanism of emulsion polymerization.

**Keywords** Droplet formation • Emulsion polymerization • Thermodynamics

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## 1 Introduction

Mass transfer is an important issue in any kind of heterogeneous chemical and physical transformation, regardless of the nature of the dispersed and continuous phase, which can be gaseous, liquid, or solid. Fundamentally, thermodynamics controls mass transfer, that is, it determines whether or not it is long lasting or even possible at all. Note that colloidal systems may be composed of any kind of material in an arbitrary state of matter, except for the gas–gas combination. The context of dispersity and heterogeneity requires that the material forming the dispersed phase is insoluble/immiscible in the continuous phase.

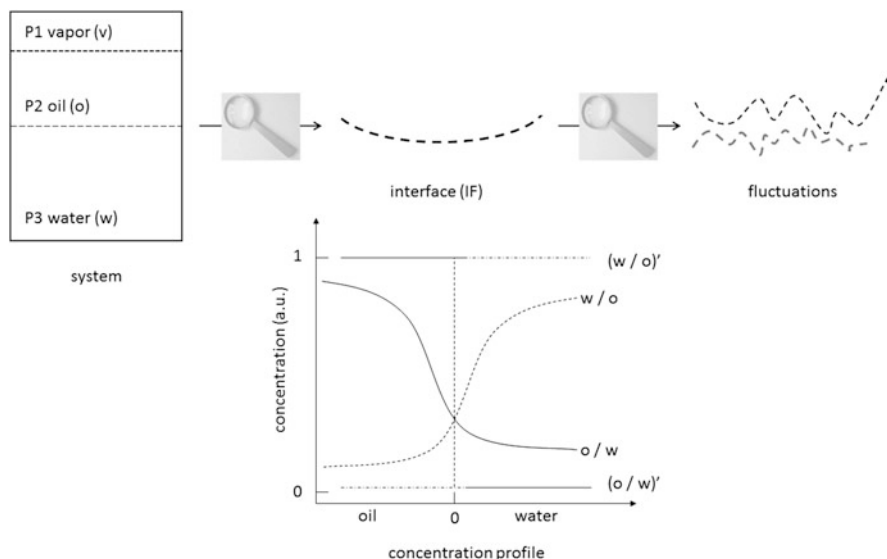
Mixing, which is the combination of matter via the input of mechanical energy, is a basic chemical unit operation [1]. If the mixture is stirred, mixing competes with thermodynamics, particularly during heterogeneous reactions where mixing enhances mass transfer, increases reaction rate, and contributes to unify product quality. However, heterogeneous reactions are also possible in the quiescent state (i.e., without any mechanical power input). Interestingly, even solid state reactions can be conducted in the quiescent state and, surprisingly, some continue until complete conversion [2–5]. Study of reactions that are commonly carried out in stirred reactors under quiescent conditions (e.g., heterophase polymerizations) allows a different and deeper insight into the mechanism.

Input of mechanical energy (i.e., forced mixing) increases the energy content in the system and, consequently, the changes introduced while stirring do not last when stirring is stopped. In other words, a stirred system is not in an equilibrium state and the application of equilibrium thermodynamics is not straightforward. Moreover, a considerable portion of the mechanical energy used for mixing is wasted as heat [6].

In contrast, changes in the quiescent state (i.e., simply by contact between two components) happen spontaneously and are almost entirely driven by thermodynamics. These changes last forever, provided the system is closed and properly sealed.

This paper aims to deliver an insightful, perceptive, and in some aspects an “out of the box” way of looking at various phenomena and issues of mass transfer that are more or less directly related to aqueous heterophase polymerization. We present a combination of experiments, thoughts, and theoretical considerations on the behavior of colloidal objects (particles and droplets) subjected to conditions allowing mass transfer.

Figure 1 sets the scene and schematically explains key aspects of our ideas for a heterogeneous fluid system. The equilibrium between both phases is established across the interface and, so, it seems reasonable to take a closer look at the interface. The interface between fluid phases, here water and an organic liquid, is not smooth or sharply defined down to the molecular level. Moreover, fluctuations lead to roughness of the interface with changing curvature, which, in turn, causes pressure according to the Laplace equation. The crucial consequence of this scenario is that the concentration profile is not a vertical step function but a more or less



**Fig. 1** Sketch of the scene at the interface between two fluids; the system is closed with respect to mass transfer with the environment. Fluid phases are ordered with decreasing density from bottom to top including the vapor phase, which is present in almost all real cases. The interface is typically not flat but curved, where the curvature is determined by the interfacial tension and characterized by fluctuations that are not constant with respect to frequency and intensity. The *lower graph* illustrates the concentration in a region close to the interface, showing that the concentration might be higher nearer the interface than farther away, where the concentration approaches the formal overall solubility

continuously decreasing/increasing profile with gradual changes in the concentration of both water and oil on the opposite sides of the interface. In this “thought experiment,” the concentration close to the interface is higher than the overall mutual solubility of both liquids in each other; hence, a supersaturation is defined in this region. This scenario should hold for any interface between two fluids and is useful for describing the transfer of matter, as explained below. These ideas are not restricted to pure fluids; they are also applicable to solutions and, in some cases, to solid–fluid interfaces. Examples of mass transfer in solid–fluid systems are the dissolution of solid polymers [7, 8], swelling of solid polymers such as hydrogels [9–11], and decomposable salts such as ammonium carbonate salt [12, 13].

## 2 Forced Droplet Formation

Stirring is used to facilitate and accelerate mixing, homogenization, and/or dissolution during chemical or physical processes. In addition, the state of mixing in a reaction vessel (or the hydrodynamic force field) can influence the result of a

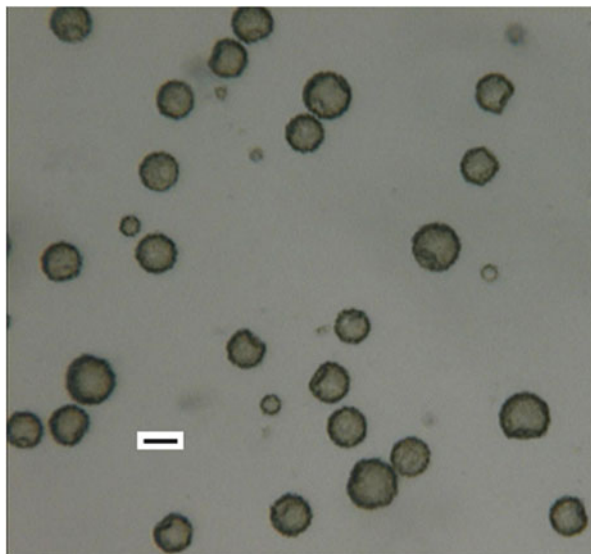
chemical reaction. Homogenization can occur with respect to the spatial distribution of heat and matter; that is, it ensures distribution of temperature and concentration evenly across the reaction volume. Because of the increase in overall interface, the exchange of matter and heat is increased. During mixing, the distribution, dispersion, and diffusion of matter are important partial steps, which take place consecutively [6, 14]. The distribution of matter along the streamlines of the mixing device is superimposed by turbulent erratic motion of larger eddies (roughly of the size of the stirrer diameter), which break into smaller eddies by dispersion. These small eddies spin and facilitate the transfer of matter, whereby their size limits the homogeneity of the reaction mixture. The size of the smallest eddies is, according to Kolmogorov, given by the power input related to the reaction mass and is called the Kolmogorov length,  $\lambda = \left(\frac{\nu^3}{P_m}\right)^{\frac{1}{4}}$ , where  $\nu$  is the kinematic viscosity and  $\lambda$  the size of the turbulence element [15]. Mixing on a length scale below  $\lambda$  requires mutual diffusion of the components. Typically, for  $\lambda$  between 30 and 100  $\mu\text{m}$ , the time for achieve micromixing is given by  $\tau_m = \frac{\lambda^2}{\tilde{D}}$ , with  $\tilde{D}$  being the diffusion coefficient; the time needed is in the order of seconds.

Cutting of matter during comminution strongly depends on the reactor volume-related power input ( $P/V$ ) and is not very dependent on the stirring rate. The stirring rate needed to attain a given  $P/V$  value varies with the size of the reactor [6].

The hydrodynamic force acting on particles during stirring in reaction vessels is, in many cases, of paramount importance. Here, “particle” is used in the very general sense as colloidal object, in either a gaseous, liquid, or solid state of matter, dispersed in a fluid, preferentially a liquid continuous phase. Stirring can lead to formation of the intended dispersions (gas in liquid, liquid in liquid, or solid in liquid). In a system as sketched in Fig. 1, the distribution, dispersion, and diffusion occur not only between the two liquid phases but also in the vapor phase. Vapor is distributed within the liquids by the action of the stirrer. Depending on the composition of the vapor phase, the presence of gas in the liquid can influence the outcome of polymerization [16]. Also, during chemical reactions, different degrees of mixing can lead to different reaction products, particularly for autocatalytic, consecutive, and parallel reactions [17, 18].

Shear forces cause mechanical stress in matter, which might be crucial for dispersing solid particles. According to Isaac Newton “*Quantitas motus est mensura ejusdem orta ex velocitate et quantitate materiae conjunctim*” (definition II in [19]), “the magnitude of the motion (i.e., the impact) is measured by the velocity and the size of the matter interplaying.” Clearly, this is important for emulsions and suspensions because the momentum (product of mass and velocity) between eddies and/or particles of the dispersed matter can be quite high and possibly result in physical action (destruction). There are many examples known where solid particles and even dissolved polymers are damaged during intense stirring. Figure 2 shows an example of polystyrene particles damaged by stirring.

**Fig. 2** Damaged polystyrene particles after being magnetically stirred in water during redispersion after centrifugational cleaning of the suspension obtained during dispersion polymerization in a toluene–butanol mixture with poly(vinyl pyrrolidone) as steric stabilizer; the *scale bar* indicates 10  $\mu\text{m}$



There are many examples of how the input of mechanical energy during chemical engineering operations affects the molecular weight distribution of dissolved polymers. Scission of polymer chains (poly(methyl methacrylate), poly(iso-butylene), polystyrene) occurs in stirred solution [20, 21]. For a given polymer, the scission rate is higher and the final chain length shorter in good solvents (where polymers possess higher hydrodynamic volume) than in poor solvents [22, 23]. This clearly points to the influence of the momentum transfer (momentum flow) from the stirrer during encounters between eddies and polymer coils [24]. Degradation of linear poly(acryl amide) was observed when the polymer solution was injected into electrophoretic channels at flow rates as low as 1  $\mu\text{L}/\text{min}$  [25]. Moreover, molecular weight degradation of polymers is a crucial issue in a variety of practical situations such as turbulent drag reduction [26, 27], the use of polymers during secondary oil recovery [28], characterization of polymers (rheology measurements at high shear rates and even size-exclusion chromatography) [29], microfluidic application of polymer solutions [28], and sonication [30].

However, stirring of suspensions can also lead to unexpected and exciting results. A prominent example is the observed symmetry-breaking in stirred crystallization experiments. Non-stirred nucleation of sodium chlorate from aqueous solutions leads to statistically equal fractions of both enantiomers. However, stirring during crystallization leads to the result that 99% of the crystals have the same handedness, although dominance of the L- or D-enantiomer is random [31–33]. The reason for this effect is mechanical damage to early-formed crystals and the action of the debris as seed particles for secondary nucleation [34].

During heterophase polymerization, transition from emulsion to suspension occurs and each state may have a different stirring requirement (see Fig. 2, showing damage to large polystyrene particles). In recent studies, we have investigated the

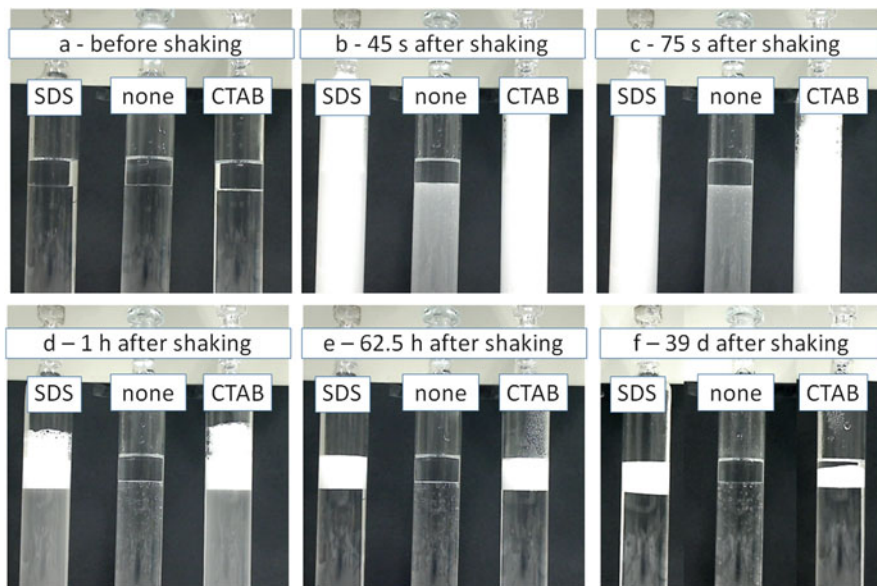
particular role of stirring during emulsion polymerization [35–37]. Experimental data evidence the occurrence of direct encounters between particles and monomer drop during polymerization. These encounters are enabled and facilitated by stirring and are crucial for fast replenishment of the consumed monomer in polymerizing particles. Diffusion of molecularly dissolved monomer in the water phase from the droplets to the particles is much too slow to compete with the fast consumption of monomer. Diffusion alone cannot maintain a high monomer concentration in the particles during the course of polymerization [38]. The impact between polymer particles and monomer phase can be so strong that the particles are pushed into the monomer, provided that the stabilizer layer is dilute enough and unable to prevent the uptake of polymer particles, which is thermodynamically favored [37]. The uptake of polymer particles by the monomer phase is thermodynamically favored in cases where the monomer is a solvent for the polymer.

These findings challenge the state-of-the-art view that, during emulsion polymerization, the monomer drops only have a passive role as monomer storehouse and that the monomer concentration within the polymerizing particles is kept constant simply by diffusion of monomer molecules through the water phase from the monomer droplets [39, 40]. The idea of a passive role for monomer drops dates back to the pioneering paper by Harkins on the mechanism of emulsion polymerization [41]. Our experimental results support the idea of shear-induced mass transfer of monomer from the droplets to the particles during emulsion polymerization. Accordingly, the transfer takes place via droplet–particle collisions, driven by the impact of the stirring energy, in a kind of momentum flow [24, 42].

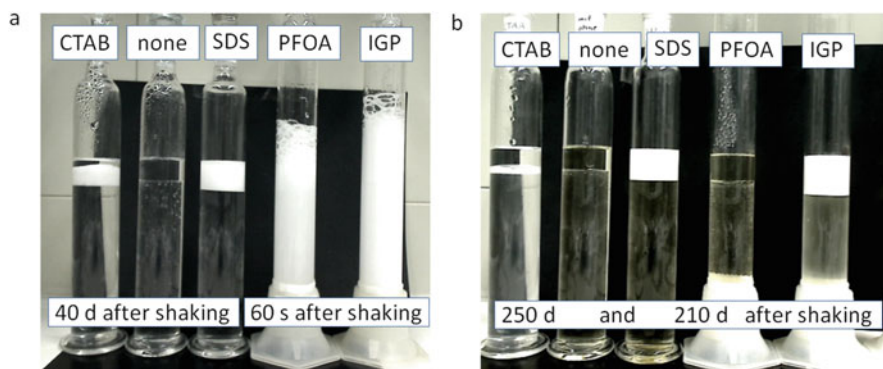
We now consider another aspect that is particularly important for emulsification. The homogenization of fluid mixtures by stirring is a process that requires a certain length of time to reach steady state with respect to a minimum average droplet size. The steady state is characterized by a dynamic equilibrium between re-breaking of larger drops, in the vicinity of the stirrer, and re-coalescence of smaller droplets farther away from the stirrer [43, 44].

The question should be asked: What happens after switching off the stirrer? As the additional energy input ends, the system relaxes and returns to the state illustrated in Fig. 1, just before starting the comminution. However, for a given oil phase, what and how fast it happens depends on whether a stabilizer is present and, if present, its properties and concentration (Figs. 3 and 4). In these experiments, ethyl benzene was the oil phase, the aqueous phase contained either a surfactant or no surfactant, and stirring was performed by shaking the properly sealed glass vials for about 30 s.

Macroscopic observation of this simple experiment with the naked eye reveals surprising results. Phase separation is not complete, even after a resting time of more than 200 days, particularly for samples containing SDS, CTAB, and IGP as surfactant. It should be stressed, again, that the systems is nonreactive and closed with respect to exchange of matter with the environment; that is, the vials are sealed and exchange of matter is only possible between water, ethylbenzene, and vapor. Interestingly, the upper oil phase shows the whitish appearance of an emulsion, but



**Fig. 3** Time sequence of the relaxation of an ethyl benzene-in-water emulsion after comminution: (a) the starting situation, with ethyl benzene on top of the aqueous phase containing 1% sodium dodecylsulfate (SDS, *left vial*), no surfactant (*middle vial*), or 1% cetyltrimethylammonium bromide (CTAB, *right vial*); (b–f) after resting time of (b) 45 s, (c) 75 s, (d) 1 h, (e) 62.5 h, and (f) 39 days



**Fig. 4** Time sequence of the relaxation of ethyl benzene-in-water emulsions after comminution. Vials contained the following additives: (a) 1% CTAB (*left vial*), no surfactant (second vial from *left*), or 1% SDS (third vial from *left*), all three after 40 days of resting time; 0.5% sodium perfluorooctanoic acid (PFOA, fourth vial from *left*), or 0.1% of a nonionic surfactant (nonylphenol ether with 15 ethylene oxide groups condensed at the *para* position, IGP), these two after 60 s of resting time; (b) the vials 210 days later

not the lower water phase. Comparing the thickness of the oil layers proves that the whitish appearance is due to a water-in-oil emulsion. Figure 4b shows that the thickness of the oil layer increases from the surfactant-free sample over the sample with CTAB to the sample with SDS in accordance with amount of emulsion phase in the layer. The thickness of the emulsion layer in the oily phase for the sample with CTAB decreases slowly with time (Figs. 3e, f and 4a, b), which indicates that the system has not yet reached thermodynamic equilibrium.

The long-lasting existence of an emulsion in the oil phase, probably a water-in-oil emulsion, is surprising because it is in contradiction to Bancroft's rule, which states that "the liquid in which the stabilizer has a higher solubility forms the continuous phase" [45].

The surfactant-free system and the system containing perfluorooctanoic acid (PFOA) eventually lead to apparent macroscopic phase separation. Interestingly, both samples phase-separate within about 1 h. This is a result of the facts that both water and ethyl benzene are not fluorophilic and that, apparently, PFOA likes water more than ethyl benzene.

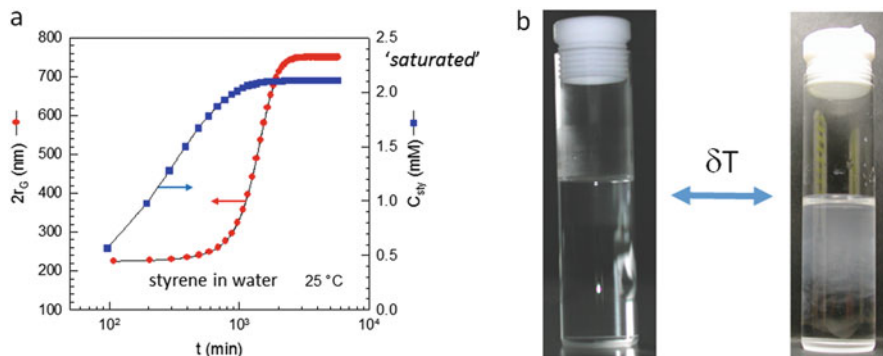
Notably, observation of the supposed formation of a water-in-oil emulsion in the oil phase with SDS, CTAB, and IGB is not possible during the emulsification process but only during de-emulsification under quiescent conditions with respect to stirring. However, we can assume that it might also happen during the emulsification stage in larger monomer drops.

### 3 Spontaneous Droplet Formation

Besides the input of mechanical energy to a system (as sketched in Fig. 1), droplet formation can also be driven entirely by thermodynamics. This process is called spontaneous emulsification and was discovered during studies of particle nucleation using multi-angle laser light scattering (MALLS) [46]. This finding was absolutely unexpected and did not result from careful planning, but rather arose serendipitously. In essence, we used MALLS to observe the styrene concentration in water during the equilibration period. We slowly and carefully placed styrene on top of water in the MALLS cuvette, in a thermostat at 25°C, and increased scattering intensity over several hours. Evaluation of the MALLS data showed that the droplet size distribution was very broad and that the average size increased with time before it leveled off after about 1,000 min, for the particular conditions during the MALLS experiments [46]. It is important to emphasize that the drop formation takes place before polymerization, just after carefully layering styrene on water to allow concentration-wise equilibration between both liquids via diffusion. The average drop diameter was greater than 1  $\mu\text{m}$  (Fig. 5) and, thus, direct observation with optical microscopy was possible.

We observed spontaneous emulsification in the interfacial region for all combinations of not completely miscible liquid pairs. Moreover, the interface between two immiscible liquids is not static but highly dynamic, with fluctuations occurring



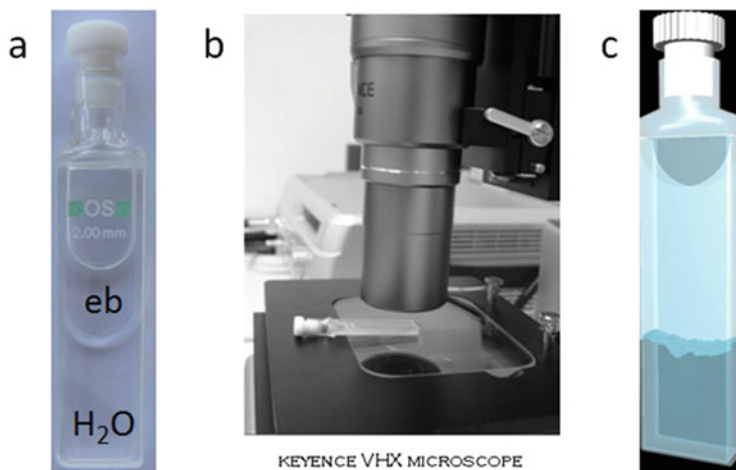


**Fig. 5** (a) Spontaneous emulsification at the styrene–water interface, as observed during the equilibration period investigated by MAALS (squares  $2r_G$ , scattering volume focused in the water phase), and the styrene concentration in water ( $C_{STY}$ , obtained by gas chromatography of the water phase). (b) Images of the aqueous phase at the end of the experiment subjected to small temperature fluctuations ( $\delta T$ ): *left* fluctuations below the equilibrium temperature, *right* fluctuations above the equilibrium temperature

as sketched in Fig. 1. Droplet formation occurs on both sides of the interface and the shape of the interface changes with time. Moreover, changes in drop size distribution and drop number take place over long periods of time. Interestingly, the scattering intensity observed during the equilibration period depends on the gas content in the system, such that degassed liquids give higher scattering intensity than gassed solutions [46].

The styrene droplet size (expressed as  $2r_G$ ) in water, as determined by MALLS, and the gross styrene content in water ( $C_{STY}$ ), as determined by gas chromatography, show an interesting correlation [46, 47]. The averaged time-dependent data sets are depicted in Fig. 5a and show that the average droplet size increases sharply in the vicinity of the saturation concentration. Over the entire concentration range,  $d(2r_G)/dC_{STY}$  (not shown) increases by a factor of about 1,000. This behavior strongly resembles critical phenomena in the vicinity of phase transition points [48].

Figure 5b illustrates the behavior of the saturated aqueous phase when the temperature fluctuates slightly below and above the equilibration temperature. This behavior shows that a styrene-in-water solution (or any other solution) close to saturation with respect to concentration is in a critical state and that macroscopic phase separation can be triggered by minor temperature fluctuations. One should be aware that a saturated solution of A in B is thermodynamically on the edge of the stability–instability limit and, hence, small changes in the thermodynamic parameters may cause phase transitions. Because the white light of an optical microscope is able to initiate polymerization (cf. Sect. 4) and the chemical changes drastically influence distribution with respect to dynamics and equilibrium state, observation of spontaneous emulsification with nonpolymerizable oils and water is much more revealing.

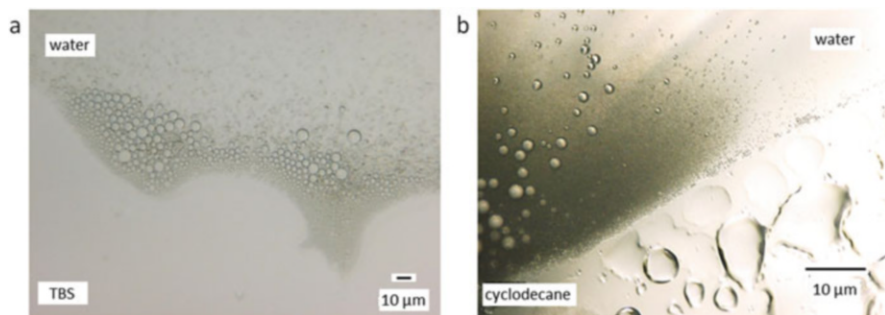


**Fig. 6** Investigation of spontaneous emulsification using optical microscopy: (a) optical cuvette filled with water and ethyl benzene (*eb*); (b) cuvette placed under the objective of the optical microscope; note that the cuvette is slightly inclined from the stopper toward the bottom; (c) drawing of the ruffled interface between water and oil (not to scale)

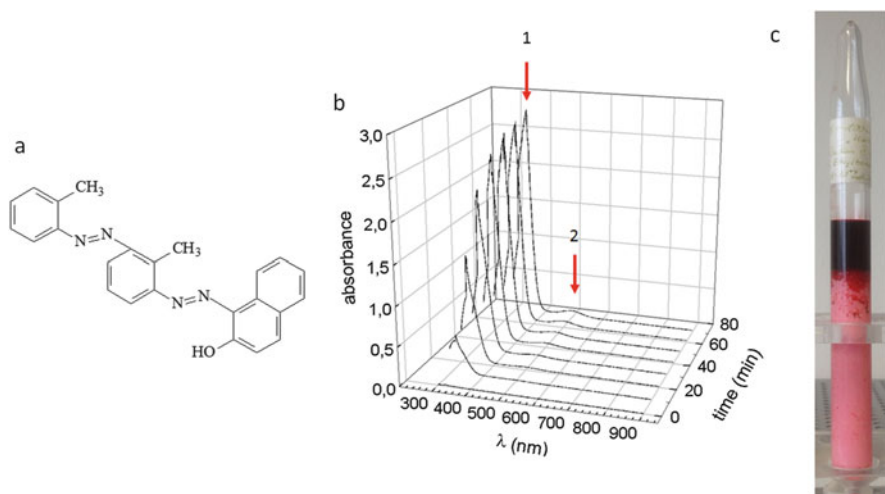
Investigations with optical microscopy were carried out as illustrated in Fig. 6. Both liquids were placed in optical cuvettes (1–10 mm thick), with decreasing density from bottom to top. The cuvettes were closed with plastic stoppers for short-term investigations but with glass stoppers and glued glass caps for permanent storage of the samples.

Figure 7 shows optical microscopy images illustrating spontaneous emulsification in *ter*-butylstyrene (TBS) and cyclodecane–water systems. The images were taken about 65 h and 6 years after establishing contact between the oil and water. The sample with TBS started to polymerize after a few days and the transparent system turned into a milky-white latex. Drop formation happened quite fast, particularly for the cyclodecane–water combination. Moreover, the time scale up to years indicates that the drops are surprisingly stable.

Droplet formation occurs on both sides of the interface, as shown in Fig. 7b. Cyclodecane drops are visible in the water phase and water drops in oil phase. If one of the liquids is water, the larger water drops adopt a nonspherical shape and adhere to the glass wall of the cuvette. The oil drops in the water phase are spherical and show, depending on the drop size, Brownian motion. There is another observation worth mentioning: Droplets are concentrated in the vicinity of the interface, but do not re-enter the corresponding mother phase, at least we have no experimental indication that this process occurs. The droplets on both sides of the interface are stable (for up to 9 years) and one might cautiously conclude that the situation shown in Fig. 7b represents a snapshot of the equilibrium state. The droplets, once formed, exist in a closed system seemingly endlessly.



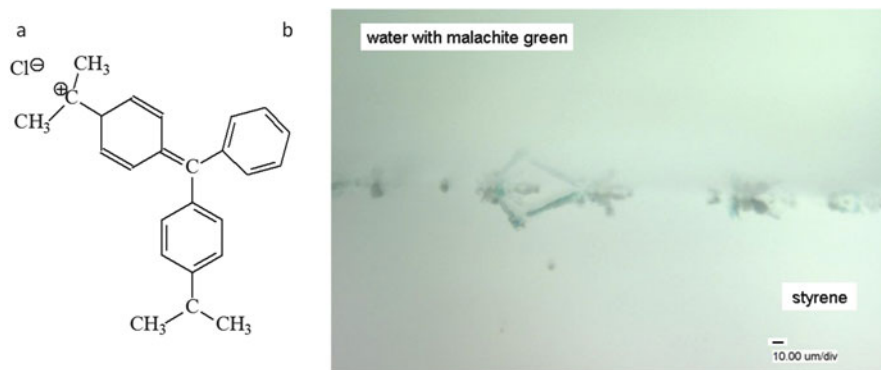
**Fig. 7** Optical microscopy images proving spontaneous emulsification for (a) *ter*-butylstyrene (taken 65 h after contact) and (b) cyclodecane–water system (taken 6 years after contact); note that the cuvette is inclined toward the water phase



**Fig. 8** Tinting polystyrene latex particles *red* with Sudan IV (a) dissolved in ethyl benzene and placed on top of the latex. (b) Dye uptake was monitored with a UV-vis immersion probe in diluted latex. The latex phase was gently stirred without generating oil drops, as described and discussed [50]. *Arrows* indicate the absorption of ethyl benzene (1) and the dye (2) at about 310 and 480 nm, respectively. (c) Image of latex overlaid with the dye solution confined in a sealed glass vial, taken some years after establishing the contact

The extent of spontaneous emulsification without any chemical transformation leads to emulsions with low volume fractions on either side. The volume fraction of the emulsion depends on the mutual solubility of the components and, for the combination styrene–water, is clearly below 1%. However, the situation changes if polymerization takes place [49].

Spontaneous emulsification also takes place with immiscible solutions, meaning that solutes from the organic phase are transferred into the water phase (and vice versa). This is demonstrated in Fig. 8, which shows that polystyrene particles are



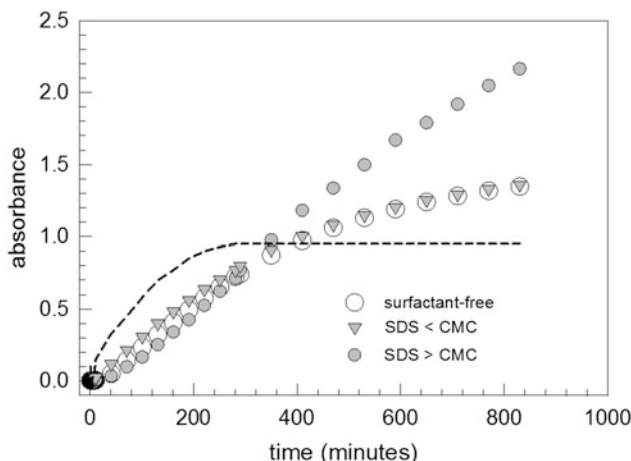
**Fig. 9** Light microscopy image (true colors) of malachite green crystals at the interface between the dye-in-water solution and styrene; the crystals are in the organic phase close to the water side and mirrored at the interface; *scale bar* marks 10  $\mu\text{m}$

slowly tinted red over a long period of time when a solution of Sudan IV (hydrophobic dye) is placed on top of the latex.

If the water phase contains surfactants, the formation of oil drops is faster and their size decreases with increasing surfactant concentration [49]. However, if just a simple (i.e., not surface active) salt is dissolved in water, the compound precipitates at the water–oil interface. In some cases, the resulting structure, together with the mirror images reflected from the interface, looks quite fancy (Fig. 9). The fact that precipitation occurs in a region close to the interface supports the sketch of Fig. 1 with respect to the distribution of the concentrations in the interfacial layer.

Another important point concerning the mechanism of emulsion polymerization should be mentioned. The occurrence of spontaneous emulsification directly touches the issue of monomer-swollen micelles and leads, at least in our understanding, to a modified interpretation of solubilization.

According to the data given in Fig. 10, we should not consider monomer-swollen micelles as being in a thermodynamically well-defined state (i.e., with a given size and amount of imbibed monomer molecules). To justify this conclusion, consider an aqueous surfactant solution with a concentration of about the critical micelle concentration (CMC). The addition of some monomer drops to this solution pushes the free surfactant concentration below the CMC. Thermodynamics requires an adsorption equilibrium of the surfactant at all interfaces. Hence, because of the broad size distribution of monomer drops with a high number concentration in the size range below 1  $\mu\text{m}$  (Fig. 5a) [46, 49, 51], “swollen micelles” with a saturated surfactant layer disappear and transform into small monomer drops. The situation is similar to Ostwald ripening, where larger particles grow at the expense of smaller ones. This idea is supported by the data summarized in Fig. 10, which prove the spontaneous transfer of toluene into the aqueous phase. Persisting swollen micelles would lead to saturation of the absorption after the time needed for equilibration, as indicated by the dashed line. However, the experimental data do not support this



**Fig. 10** Increase in absorption of the aqueous phase (measured at  $\lambda = 260$  nm, the long-wave absorption maximum of toluene) during sorption of toluene in pure water (*open circles*), in SDS solution with concentration below the critical micelle concentration (CMC) (0.43 g/L, which is about 1/6 CMC, *grey circles*), and above the CMC (5.3 g/L, which is about twice the CMC, *grey downward triangles*). The *dashed line* indicates the expected course, assuming swollen micelles with both fixed size and fixed imbibed amount of toluene. Measurements were carried out at a temperature of 23°C in 1-cm UV cuvettes containing aqueous phase and a carefully placed toluene layer on top. The water layer in the cuvette was much higher than the optical path of the Uvikon 931 spectrometer (Kontron Instruments, UK)

idea but, instead, show increasing absorption in all cases, which means ongoing oil transport to the aqueous phase. In addition, the data prove the facilitating action of high surfactant concentration on spontaneous emulsification.

The experimental facts are quite clear, but a satisfying understanding of what causes spontaneous emulsification and of its driving force is still lacking. To achieve this, one has to distinguish between the thermodynamic driving force for droplet formation and the formation mechanism itself. A thermodynamic justification of spontaneous emulsification seems possible, as follows: Immediately after contact between the oil phase (o) and water (w), mass transfer of oil molecules into water and of water molecules into oil starts. The chemical equilibrium of the system, as sketched in Fig. 1 (no mass transfer with the environment and neglecting the vapor phase), is reached when the chemical potential ( $\mu$ ) for a given liquid is the same in each of the liquid phases. In the following equations, the subscript letter denotes the liquid and the superscript letter denotes the phase. For example,  $\mu_o^w$  and  $\mu_w^o$  represent the chemical potential of oil in the water phase and of water in the oil phase, respectively. Zero after a subscript letter indicates the concentration of pure liquid (i.e.; the reciprocal of molar volume  $v_m$ ). In Eq. (1), the chemical potential ( $\mu$ ) for a given liquid is the same in each of the liquid phases, indicating chemical equilibrium.

$$\mu_o^o = \mu_o^w, \mu_w^o = \mu_w^w \quad (1)$$

Applying standard thermodynamics and considering homogenous phases after equilibration, equalities (2a) and (2b) are obtained for the oil and water, respectively.

$$\mu_o^o = \mu_o^w = \mu_{o,0} + RT \ln \frac{C_o^o}{C_{o,0}} = \mu_{o,0} + RT \ln \frac{C_o^w}{C_{o,0}} \quad (2a)$$

$$\mu_w^o = \mu_w^w = \mu_{w,0} + RT \ln \frac{C_w^o}{C_{w,0}} = \mu_{w,0} + RT \ln \frac{C_w^w}{C_{w,0}} \quad (2b)$$

Considering the experimental values for the mutual solubilities of styrene and water,  $C_w^o = 4 \times 10^{-2}$ M,  $C_o^w = 3 \times 10^{-3}$ M [52], we get the values  $C_w^w = 55.32$ M,  $C_o^o = 9.993$ M. Here, we assume that the molar volumes of water and oil are 18.07 and 100 mL/mol, respectively. The estimated concentrations  $C_w^w$  and  $C_o^o$  take into account the presence of the corresponding solute. Applying these values in (2a) and (2b) shows that the equilibrium conditions (1) are not fulfilled because the chemical potentials of the mother phases are much higher than those of the complementary phases. A way out of this dilemma is to consider heterogeneity, that is, formation of an emulsion on either side instead of formation of a homogeneous solution. The key is that emulsion drops lead to a size-dependent increase in chemical potential [35, 53, 54]. With this, the chemical potentials can be expressed as shown in (3a–3d).

$$\mu_o^o = \mu_{o,0} + RT \ln \frac{C_o^o}{C_{o,0}} + RT \frac{k_{1,o}^o}{d_{d,w}^o} \quad (3a)$$

$$\mu_o^w = \mu_{o,0} + RT \ln \frac{C_o^w}{C_{o,0}} + RT \frac{k_{1,o}^w}{d_{d,o}^w} \quad (3b)$$

$$\mu_w^w = \mu_{w,0} + RT \ln \frac{C_w^w}{C_{w,0}} + RT \frac{k_{1,w}^w}{d_{d,o}^w} \quad (3c)$$

$$\mu_w^o = \mu_{w,0} + RT \ln \frac{C_w^o}{C_{w,0}} + RT \frac{k_{1,w}^o}{d_{d,o}^o} \quad (3d)$$

The constants  $k_1$  derive from the corresponding Laplace relations (4a–4d), where  $\sigma$  is the interfacial tension,  $R$  the gas constant, and  $T$  the temperature. The interfacial tensions for the oil drops in water and the water drops in oil phase are assumed identical.

$$k_{1,o}^o = \frac{4\sigma \times v_{m,w}}{RT} \quad (4a)$$

$$k_{I,o}^w = \frac{4\sigma \times v_{m,o}}{RT} \quad (4b)$$

$$k_{I,w}^w = \frac{4\sigma \times v_{m,o}}{RT} \quad (4c)$$

$$k_{I,w}^o = \frac{4\sigma \times v_{m,w}}{RT} \quad (4d)$$

The equilibrium conditions for the oil and the water lead to the inequalities (5a, 5b), which allows derivation of a relation between the size of oil drops in the water phase and water drops in the oil phase (6).

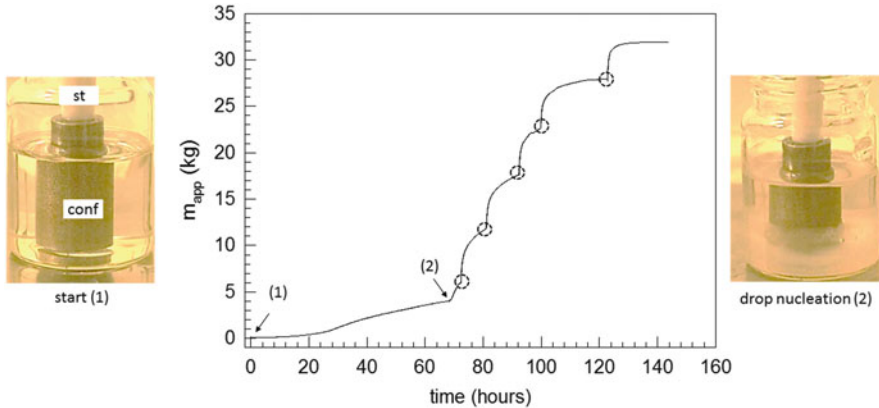
$$\ln \frac{C_o^o}{C_o^w} = \left( \frac{k_{I,o}^w}{d_{d,o}^w} - \frac{k_{I,o}^o}{d_{d,w}^o} \right) > 0 \quad (5a)$$

$$\ln \frac{C_w^w}{C_w^o} = \left( \frac{k_{I,w}^o}{d_{d,w}^o} - \frac{k_{I,w}^w}{d_{d,o}^w} \right) > 0 \quad (5b)$$

$$d_{d,o}^w \approx \frac{v_{m,w}}{v_{m,o}} d_{d,w}^o \quad (6)$$

Assuming the data for water and styrene, Eq. (6) suggests that the water drops are about 1.8 times larger than the oil drops in water. Because the drops in both phases possess a very broad size distribution, the average drop size is only a very rough measure. Nevertheless, the largest water drops are bigger than the largest oil drops (Fig. 7b), which supports the above thermodynamic argument with respect to the driving force of spontaneous emulsification. The nucleation of drops takes place close to the interface, which supports the idea that classical nucleation theory can be applied to describe the droplet formation mechanism.

A way to prove these ideas experimentally is a swelling experiment, as described next. The experiment also supports the idea that monomer droplets play a major role in latex particle swelling. A method for measuring swelling pressure has recently been developed in our laboratory [55] and was applied here. A crosslinked bulk polystyrene sample was placed in a confinement (ensuring almost isochoric conditions) with porous walls, allowing contact with an outer liquid phase, which is inside a container placed on a balance. The confinement containing the sample has contact with the container bottom and, hence, any action on or of the sample is transferred directly to the balance, easily allowing monitoring of an apparent mass change ( $m_{app}$ ). We emphasize that the method measures the “desire” to establish direct contact between the sample and the fluid surrounding the confinement. Figure 11 shows the development of the balance readout over the whole duration of the experiment. This particular experiment was designed on the basis of Okubo’s dynamic swelling method, with changing composition of the continuous phase [56, 57].



**Fig. 11** Changes in the balance readout during a swelling pressure experiment. Crosslinked polystyrene was placed in the confinement (*conf*) with a stamp (*st*); (1) marks the time when a mixture of toluene and ethanol (30/70 vol%) was added; (2) indicates when water was added (after about 70 h), which caused the transition from solution to emulsion. The *left* images show the setup at (1) and the *right* image after (2), when water drops are clearly recognizable in the lower part of the liquid. *Circles* mark the time when the limit of the balance was reached and the load was manually relaxed (the curve is the sum of individual sections after each relaxation)

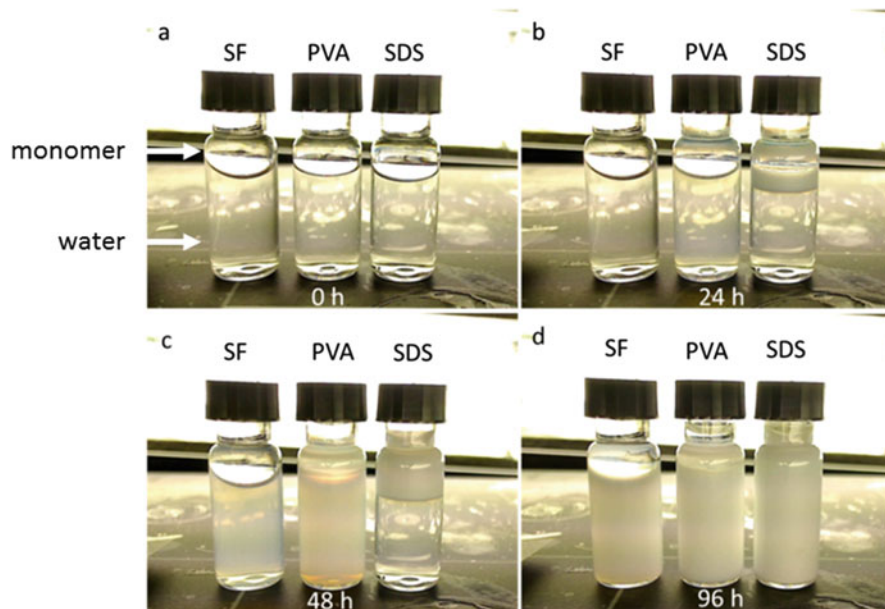
The data in Fig. 11 show only a slight increase in the balance readout in the presence of toluene/ethanol solution. However, after water addition and the formation of toluene droplets, the swelling pressure increased sharply due to the presence of toluene drops, which have a higher toluene concentration than the solution. These droplets cause a stronger “desire” for the polystyrene in the confinement. This is in accordance with the swelling results obtained with forced swelling [36].

## 4 Spontaneous Emulsification and Heterophase Polymerization

Knowing that spontaneous emulsification takes place, it is straightforward to check what happens when the oil phase is a polymerizable monomer such as styrene. The use of styrene allows initiator-free photoinitiation, which happens inside monomer drops because more than one styrene molecule is necessary to initiate the polymerization [58]. Of course, the setup as shown in Fig. 12a also leads to initiation in the styrene phase.

Figure 12 shows the time sequence of such polymerizations under different stabilizing conditions, leading to significant differences in the appearance of the reaction system. The common result for all systems is formation of polymer particles in the aqueous phase (latex formation) and a polymerized monomer layer. Astonishingly, the appearance of the monomer phase during polymerization strongly depends on the stabilizer. At the end of the polymerization, only for



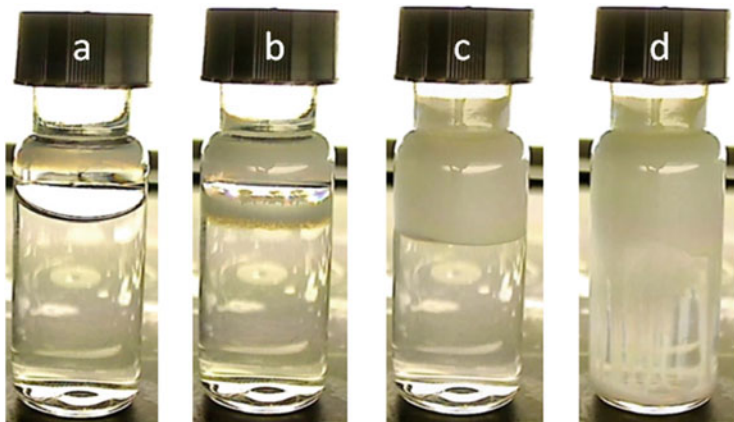


**Fig. 12** Time sequence of images illustrating self-photoinitiated styrene polymerization after (a) placing the monomer phase on top of the water phase and (b) 24 h, (c) 48 h, and (d) 96 h later; *SF* surfactant-free, *PVA* poly(vinyl alcohol), *SDS* sodium dodecylsulfate as stabilizer (1% by weight in the aqueous phase). The photopolymerizations were carried out at room temperature by placing the reaction vials in front of normal fluorescence tubes used for laboratory illumination (Osram L 18 W, light color 840, lumilux, cool white)

surfactant-free polymerization, the monomer phase resembles that of a bulk polymerization (i.e., a transparent glassy state).

In our opinion, this is the most interesting result. The styrene phase is almost completely transparent during the entire duration of the reaction in the absence of stabilizer. However, in the presence of SDS, a typical stabilizer for emulsion polymerization, the polymerization starts in the monomer phase with formation of an emulsion phase visible by its turbidity (Fig. 13). With poly(vinyl alcohol) (PVA) as stabilizer, appearance of the monomer phase is between that of the other cases. After 48 h of polymerization time, the aqueous phase of the polymerization with PVA is much more turbid than in the other cases. Particularly for the polymerization with SDS, the latex phase appears to be concentrated in the oil phase, as indicated by its increasing thickness compared with the other system (Fig. 12c). The images in Fig. 13 for polymerization with SDS elucidate this behavior, particularly the shift in turbidity from the oil toward the water phase.

The sequence of snapshots in Fig. 13 shows how the main locus of polymerization, evaluated by the turbidity of both phases, shifts from the oil toward the water phase. A turbid region in the monomer phase appears about 6 h after exposing the vial to the light source. It appears as if the “pressure of the latex” in the oil phase



**Fig. 13** Transition of turbidity from the oil to the water phase during self-photoinitiated polymerization of styrene placed on top of an aqueous SDS solution (for details see Fig. 12). The vial was illuminated for (a) 10 h 40 min, (b) 13 h 50 min, (c) 53 h 10 min, and (d) 56 h 40 min

increases with time until it breaks through the interface into the aqueous phase. However, this is a prosaic description, rather than scientific. Admittedly, a sound scientific explanation for this effect is not possible at present. It appears reasonable to assume that this behavior is related to spontaneous emulsification and, particularly, to that of water in the oil phase, supported by the action of SDS surfactant. Further investigations are necessary to reveal more details of this process.

The experimental data in Fig. 12, labeled “SF,” were obtained with pure styrene on top of pure water (i.e., the simplest possible recipe for heterophase polymerization). At this point, questions arise regarding the stabilization mechanism of the spontaneously formed drops or particles. Zeta potential measurements revealed that the particles obtained in the absence of any stabilizer had a potential of  $-47.1 \pm 1.9$  mV. This value is comparable with that measured for particles stabilized with SDS ( $-50.6 \pm 3.1$  mV) [59], but much more negative than that observed for the particles stabilized with PVA ( $-14.0 \pm 3.7$  mV). Regarding the origin of this potential, two hypotheses can be discussed. The first hypothesis, that it is a kind of contact potential, can be traced back to Alfred Coehn [60]. The second explanation is based on preferential adsorption of hydroxyl anions at the droplet–water interface, which was also observed for other nonpolar oil-in-water emulsions [61–67].

## 5 Summary

In this contribution, we look at mass transfer in heterogeneous systems, mainly from the perspective of colloid science rather than chemical engineering. Our main goal is to combine various experimental observations from study of

nonpolymerizing systems, which are all related to heterophase polymerization. Because studying these effects was only possible under experimental conditions very different from those applied in technical heterophase polymerization, direct experimental proof of their relevance and importance for technical polymerizations is not possible at this time. However, we are convinced of the importance of the results for a deeper mechanistic understanding, principally because the observed effects connect heterophase polymerization with the general context of physical and colloid chemistry. Hopefully, this discussion will initiate new studies in the future.

We focus on spontaneous emulsification as thermodynamically driven emulsion formation at a colloidal scale, which should take place under all experimental conditions, including forced emulsification processes. However, this can only be reasonably supposed and is hard to verify experimentally, because forced emulsification is always able to emulsify larger volumes.

The key aspect of our discussion with respect to mass transfer between two liquid phases is that it takes place in both directions across the interface. For the oil–water combination, this means that an oil-in-water emulsion on the aqueous side and a water-in-oil emulsion on the oily side are formed. A number of experimental results are presented that prove spontaneous emulsification.

The implications of these results for the mechanism of heterophase polymerization, particularly emulsion polymerization, will be treated in an upcoming paper dealing with simulations of mass transfer into polymerizing latex particles.

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