7
Membrane Emulsification for Food Applications

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7.1
Introduction

Membrane emulsification has attracted increasing attention to pharmaceutical, chemical, food and cosmetic industries in the last decade. As an innovative process it may provide reduction in energy, chemicals consumption and waste production [1]. Operational flexibility and reduction in the ratio of equipment size to production capacity, easy scale-up, and reproducibility may lead membrane emulsification technologies to considerable efficiency. It may be suitable for industrial-scale production as a novel process intensification, eliminating major large-scale equipments that require high maintenance costs.

Nowadays, the food industry is putting considerable effort into the manufacturing of products with high quality, nutritional value and a natural taste. Appropriate processing methods are at the core of this development, because processing determines the product microstructure to a significant extent. Moreover, delicate ingredients and structural elements can be adversely affected in their functionality and nutritional value if the processing is too harsh. In the past decades, membrane emulsification (ME) has been identified as a promising method for making single and multiple emulsions, solid lipid colloids, gel and core shell particles under relatively mild conditions [2–9]. Some recent literature has also reported the production of nano- and microbubbles using cross-flow membrane emulsification [10–14].

Several industries have been investing in the development of these technologies, which may lead to a new process route and equipment [4, 13, 15–23]. ME and microchannel emulsification (MCE) are low energy input process (10^3 to 10^6 J m^{-3}), and have the potential to produce very narrow droplet-size distribution compared to other emulsification techniques, with special application to parenteral emulsions as droplet-size distribution can be easily controlled by process parameters.

Experimental studies and modeling analysis have shown a great advance on the understanding of droplet formation and its uniform droplet-size distribution using membrane (ME) and microchannel (MC) emulsification processes [19, 24–33], which will be highlighted in Section 7.2.

Irregular microstructure and surface properties of current membranes still limit the full exploitation of the benefits of ME, where its major disadvantage is the low flow rate compared to conventional mechanical emulsification processes. Also membrane fouling by particulates or adsorbing species can be an important problem. Particulate fouling will block pores, while adsorbing species (which may even be emulsifiers from the product formulation) can change the wetting properties of the membrane. Various membrane emulsification technologies and membrane materials have been developed; current operating methods include cross-flow (XME), dead-end (PME), rotating (RME), and vibrating (VME) membrane emulsification, as well as microchannel emulsification (MCE). This chapter will describe each of these methods and their applications.

7.1.1
Cross-Flow Membrane Emulsification (XME)

XME is considered the conventional membrane emulsification process to prepare uniform droplets of oil-in-water (O/W) and water-in-oil (W/O) emulsions, and also multiple emulsions. Important process parameters to be considered in XME are: transmembrane pressure; type of membrane, permeability, and thickness; membrane pore size, porosity and wettability; type of emulsifier and its concentration; cross-flow and continuous phase velocity; viscosity of dispersed and continuous phases. In this process a relative low pressure forces the disperse phase through the membrane pores and the droplets detach from the pore outlets into the continuous phase containing an emulsifier for immediate droplet stabilization. Interfacial tension, inertial, buoyancy, dynamic lift, drag and static pressure difference forces act on a droplet during this membrane emulsification process. It is necessary to have a balance between all these forces for the success of the droplet formation [3, 9, 34–36]. Under model conditions the process can be monitored by a high-speed camera and optical microscopy.

For the production of O/W and W/O emulsions, either hydrophilic or hydrophobic membranes, respectively, are required. Examples of hydrophilic membranes include ceramic (α-Al$_2$O$_3$, zirconium oxide) and metallic, microporous glass membrane made of calcium aluminoborosilicate glass synthesized from a volcanic ash called Shirasu (CaO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$, Shirasu porous glass, SPG), polypropylene, polycarbonate, polyvinylidene fluoride (PVDF), and poly(tetrafluoroethylene) (PTFE) [37]. They can be made hydrophobic by chemical surface modification, especially organic silane coupling agents (e.g., octadecyltrichlorosilane), which are nonfood grade. A range of membrane with pore size ranging from 0.05 to 30 µm is commercially available. The pore diameter of the membrane is the crucial parameter to determine the final droplet size of the emulsion and the distance between two adjacent pores should be far enough to prevent coalescence of forming droplets. Wettability of the membrane is very important for the process performance, allowing narrow droplet-size distributions [2]. Membranes should always be wetted by the continuous phase before starting the emulsification

process. To maintain membrane performance, it is important to avoid wetting by the disperse phase.

More recently, Kukizaki [21] has used SPG membranes to study the droplet formation behavior in the absence of shear flow at the membrane surface. A faster decrease in the interfacial tension and slightly higher transmembrane pressure than the capillary pressure allowed spontaneous formation of smaller droplets with narrower size distribution.

7.1.2
Dead-End Membrane Emulsification (PME)

Suzuki *et al.* [38, 39] have reported the first research work on the application of PME to produce O/W and W/O emulsions. In this membrane emulsification technology a preliminary coarse emulsion is forced through the porous membrane and mother droplets are broken up into daughter droplets resulting in smaller droplet sizes and narrower droplet-size distributions than the pre-existing emulsion. Higher trans-membrane flux and easier operational conditions makes PME more advantageous than XME for large scales, however wider droplet-size distribution can be observed.

For the production of more monodisperse emulsions, a number of passes of the emulsion through the membrane is required, which make the process more expensive than XME.

Different types of membrane materials have been used in PME, SPG membranes are the most conventional ones. Some authors have also used PTFE [40, 41], polyamid 6,6 [42, 43]. Increase of the disperse phase fraction results in lower transmembrane pressure for any type of membrane used. As in XME, different surface properties of the membranes provide the production of either O/W or W/O emulsions (hydro-phylic and hydrophobic membrane, respectively).

Vladisavljević *et al.* [44] investigated the influence of anionic, nonionic and zwitterionic emulsifiers on the mean droplet size, transmembrane flux, and mem-brane fouling in repeated PME using SPG membrane. Control of pH may allow better performance during processing, mainly when protein is used as the emulsifier as agglomeration occurs at pHs closed to its isoelectric point, resulting in strong membrane fouling and low transmembrane flux.

7.1.3
Rotating Membrane Emulsification (RME)

Rotating disk/cylindrical membranes have been applied to dynamic membrane filtration in large scales. The success of this filtration method was the motivation for the development of the novel rotating-membrane emulsification process. More recently some research groups have shown interest in its application due to increasing in flow rate of the dispersed phase through the membrane, which single and multiple monodisperse emulsions could be successfully produced [45–49].

In this technique, shear stress is developed by rotating a cylindrical membrane and disperse phase is radially forced through its pores into the continuous phase

containing the emulsifier, allowing droplet stabilization. Vladisavljević and Williams [48] studied the production of O/W emulsions using RME at different angular speeds (50–1500 rpm). A stainless steel membrane with pore diameter of 100 μm was used, and showed the best performance at 350 rpm where droplet sizes up to 107 μm (coefficient of variation, CV = 4.9%) were produced. The literature has shown a consistent behavior of the RME process where the angular speed significantly influences the size of the droplets formed. Droplet size tends to decrease at higher angular speeds [48].

RME is a potential process to be applied in industrial scale, mainly for the production of larger droplet size [47]. Further development is required since it is a relative new membrane emulsification process

7.1.4
Vibrating Membrane Emulsification (VME)

In the previous section, membrane rotation was discussed as an alternative to cross-flow for creating a shear force on the droplets that form at the membrane pores. Membrane vibration is another option, and may be more appropriate for flat membranes like perforated metal plates and microengineered silicon wafers. Zhu and Barrow [50] have studied the effect of lateral piezoactuated vibration of thin microengineered silicon nitride membranes in a laboratory-scale rig. The formation of droplets at individual pores (with large interpore distance) was observed with videomicroscopy. In order to enable these observations the timescale of droplet formation could not be chosen too short, so crossflow and dispersed phase flow had to be kept rather small. This resulted in rather large droplets for the stationary membrane case, that is, of the order of 100 μm. Membrane vibration was observed to reduce the droplet size, but only at rather low frequency and not to a very large extent. Kelder *et al.* [19] have studied XME with vibrating membranes theoretically, using a simple analytical force-balance model as well as 3D computational fluid dynamics (CFD) simulations. These authors showed that the effect of membrane vibration on droplet formation is quite complex. First, the drag force due to the vibration should be at least comparable to the drag exerted by the crossflow in order to have a significant effect. Moreover, the frequency of the vibration should be linked to the droplet-formation frequency in order to assure that each droplet is affected by the vibration in the same way. Outside this "resonance" the droplet behavior can become quite irregular, leading to a wide size distribution. Kelder *et al.* [19] also considered the power requirements for the vibration. The average power was found to be proportional to the square of the vibration amplitude and to the third power of the frequency. The power input m^{-3} of emulsion was estimated as well, and was found to be of the order $10^5 \, W \, m^{-3}$ for typical conditions. This is significant compared to the overall energy input and diminishes the energy-efficiency advantage that is usually attributed to XME. Overall, one can conclude that membrane vibration is not an obvious option for large-scale applications, and that even for small-scale specialty applications considerable technical challenges still have to be overcome.

7.1.5
Microchannel Emulsification

Several types of ME have been introduced in the previous sections. The smallest droplet-size distribution for ME is approximately 10% in CV, primarily due to pore-size distribution and/or sensitivity to operating conditions. Monodisperse emulsions consisting of highly uniform droplets have recently received great attention in various fields including foods, pharmaceuticals, cosmetics, and chemicals. Nakajima and colleagues proposed microchannel emulsification (MCE) for producing highly uniform droplets with a small coefficient of variation of below 5% in the 1990s [51]. The droplet generation unit (DGU) used in MCE is a microchannel (MC) array consisting of parallel MCs with a terrace and a deep well (Figure 7.1a). Droplets are directly generated in the well via an MC array, even in the absence of a cross-flowing continuous phase. This droplet generation based on spontaneous transformation is a very mild process and has very high energy efficiency (e.g., 65% in Sugiura *et al.* [25]). Dead-end MCE chips were used in the initial stage of MCE researches, with Nakajima and colleagues applying MC array chips developed for analyzing blood rheology in blood capillaries [52] to emulsification. Interestingly, the terrace, which plays an important role in droplet generation by MCE, was originally designed for observing the behavior of blood components. Kawakatsu *et al.* [53] designed cross-flow MCE chips for long-term operation and emulsion collection. However, MCE chips consisting of grooved MC arrays (Figure 7.1a) have a very low productivity of vegetable oil droplets ($<1\,\mathrm{L\,m^{-2}\,h^{-1}}$) when MCs with a size of $10\,\mu\mathrm{m}$ are used. A straight-through MC array consisting of highly integrated microfluidic through-holes (Figure 7.1b) remarkably improved the droplet productivity of MCE [54]. Straight-through MC arrays with an MC size of $10\,\mu\mathrm{m}$ produced uniform vegetable oil droplets at a maximum dispersed-phase flux of $60\,\mathrm{L\,m^{-2}\,h^{-1}}$ [55]. Currently, MCE is capable of producing monodisperse emulsions with a droplet
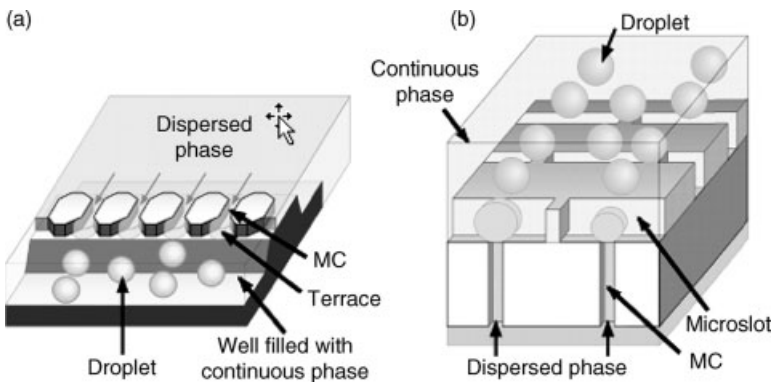
Figure 7.1 Schematic drawings of droplet generation via part of a grooved MC array (a) [51] and part of a straight-through MC array (b) [83].

size of 1 to 100 μm [56, 57]. Monodisperse emulsions produced by MCE also have been used as templates for obtaining monodisperse microdispersions such as microparticles and microcapsules. Later sections will discuss the process fundamentals of MCE and the production of emulsions and microdispersions for food applications using MCE.

7.2
Understanding of the Process at the Pore Level

The literature on droplet formation in ME and MCE is extensive, and a detailed discussion is beyond our current scope. Rather, we intend to provide a short overview of the current understanding and recent developments, referring to key papers for further details and additional references. We will subsequently discuss XME, PME and MCE.

7.2.1
XME

The growth and detachment of a droplet at a (often circular) pore in a cross-flow has been studied in detail over the last decade using high-speed videomicroscopy, computational fluid dynamics (CFD), surface evolver and lattice-Boltzmann (LB) simulations [19, 27, 33]. These studies show that the growing droplet is initially displaced from the pore in the direction of the cross-flow, while remaining attached to it by a thin neck. When the growing droplet has become too large for the neck to resist the drag force on the droplet, the neck ruptures and leaves part of its volume attached to the pore as the starting point for the formation of the next droplet. Kelder *et al.* [19] noted in their CFD simulations that the rupture of the neck occurs close to the droplet rather than close to the pore, and hypothesized that the part of the neck close to the pore is stabilized by the centrifugal force that is due to the bending of the droplet phase flow direction over almost 90°. Further down the neck this stabilizing effect has disappeared and instability can occur more easily. These and other studies have provided some quite useful insight, but it is worth noting that for experimental and computational reasons the details of the neck formation and behavior have been studied under conditions where rather large droplets are produced. It is not clear at present if all the details translate completely to the droplet size range (well) below 20 μm, which is typical for many food emulsions.

For process optimization and scale-up, the simple mechanical models that were introduced first by Schröder *et al.* [58] and Peng and Williams [24] are still preferred. These authors (and many after them) have shown that a number of forces act on the forming droplet, but that several of these are usually orders of magnitude too small to be relevant. Peng and Williams [24] have retained only the two largest contributions, that is, the drag exerted on the forming droplet by the cross-flow and the interfacial tension force that keeps the droplet attached to the pore. Their first model was a torque balance, as shown at the lefthand side of Figure 7.2. In this model the droplet is
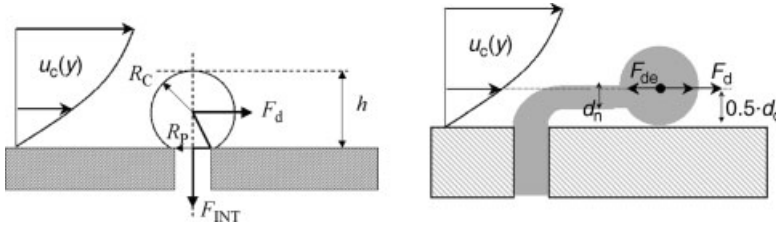
Figure 7.2 Torque balance and force-balance models, after Peng and Williams [24].

assumed to grow as a hemispherical cap on top of the pore. Peng and Williams [24] have shown that the final droplet radius R_D is then given by:

$$\left(\frac{R_D}{R_P}\right)^3 = \frac{\sigma}{5.1\,\tau_W\,R_P} \tag{7.1}$$

Here, τ_W is the wall shear stress, which is given by:

$$\tau_W = \frac{1}{2}\,\varrho f\,W^2$$

W is the relevant mean velocity, ϱ is the density and f is the friction factor, which depends on the channel Reynolds number. It is noted that this torque model does not invoke the notion of a neck. Peng and Williams [24] also briefly introduced a simple force balance, which does invoke the notion of a neck between the droplet and the pore. Near the critical conditions for detachment the neck is supposed to have bent about 90° towards the direction of the cross-flow, while more or less retaining its radius, as sketched at the right-hand side of Figure 7.2. The interfacial tension force is then comparable in magnitude to the torque case, but directed opposite to the drag force (hence a force balance rather than a torque balance). The final equation of this model is very similar to that of the torque balance, that is, the exponent 3 is merely replaced by an exponent 2. Kelder *et al.* [19] have shown that this simple force-balance model agrees fairly well with CFD simulations in which neck formation is observed. It is noted that De Luca *et al.* [59, 60] have recently developed a different force-balance model, focusing on the forces that act on the contact line on the membrane surface and without invoking the formation of a neck.

The above models refer to cases where the interfacial tension force and the drag force are dominant compared to the other forces. However, when the cross-flow velocity is reduced to (almost) zero the hydrodynamic force exerted by the liquid that flows into the droplet becomes the dominant force that leads to detachment. This regime, which is sometimes referred to as "spontaneous detachment", has been studied in detail at the University of Sofia [61, 62]. In the first paper these authors presented a detailed analysis of the hydrodynamic force exerted on the forming droplet by the liquid flowing into it. In the second paper they made an analogy between the detachment of a droplet from a pore in zero cross-flow and the gravity-induced detachment of a pending drop. In particular, they took the

well-known theory for gravity-induced detachment of a pending drop and replaced gravity by the previously established hydrodynamic force exerted by the liquid. In this way they were able to provide a consistent quantitative analysis of the droplet formation in (almost) zero cross-flow. Discussing details goes beyond the scope of this chapter, but we do note that this work explains for the first time why many authors have observed a correlation $R_C/R_P \approx 3$ over a wide range of pore sizes under conditions of transmembrane pressures just above the critical value and relatively small cross-flow. It is frequently suggested in the literature that a correlation of the type $R_C/R_P = \text{constant}$ is inherent to XME, but the wide range of reported "constants" is then difficult to understand. Moreover, one can already see in Equation 7.1 (in which a factor $1/R_P$ also appears at the right-hand side) that this linear proportionality does not hold in the presence of a non-negligible cross-flow. De Luca *et al.* [59, 60, 63] tried to modify and extend the mechanical models such that they do predict a linear correlation, but convincing results were not obtained. These authors who have reported a correlation $R_C/R_P = \text{constant}$ with a value for the constant that lies well above 3 have probably merely made a linear fit to a limited range of pore sizes.

Another extreme case is that in which the droplet phase flows out of the pore so fast that it initially becomes a jet, which breaks up into fragments at some distance from the pore. This is a well-known phenomenon for macroscopic nozzles and orifices, and Christov *et al.* [62] have shown it experimentally for liquid flowing out of a thin (180 μm diameter) capillary. Lambrich and Schubert [35] and others have mentioned the jetting regime in ME as well, and Lambrich *et al.* [64] have presented experimental results on XME in the jetting regime for microengineered membranes. As pointed out by Lambrich and Schubert [35] the main advantage of operating in the jetting regime is the large droplet-phase flux as compared to conventional XME conditions, but this can only be obtained at reasonable transmembrane pressure if (nearly) all pores can be made to produce jets. The hydrodynamic resistance per membrane channel then has to be rather small, which is fairly easy to realize for the thin microengineered membranes used by Lambrich *et al.* [64]. For a much thicker ceramic or SPG membrane this is probably not possible. Nevertheless, jetting can play a role for these membranes, as argued by Christov *et al.* [62], but this is seen in the droplet-size distribution rather than the overall flux. The proposed mechanism is that the large interconnectivity of channels within a ceramic or SPG membrane allows for the possibility that many internal channels jointly feed a given pore at the membrane surface, which then gets a high exit velocity.

Up to now we have discussed droplet formation at a single pore, neglecting interactions with neighboring pores. Whether or not these are important depends on the interpore distance (or membrane porosity). If pores are closer to each other than the critical diameter for a single pore, growing droplets can coalesce when not properly stabilized by emulsifiers or can push each other off the pore when well stabilized. The latter behavior has been observed among others by Zhu and Barrow [49] Egidi *et al.* [65] and Kosvintsev *et al.* [66]. Kosvintsev *et al.* [66] have also developed a mechanical model for the push-off effect for the case of zero cross-flow. Typically this push-off effect leads to smaller droplets, since

growing droplets then cause each others detachment prematurely compared to the single-pore case.

Another aspect that has received considerable attention in recent years is that of interfacial rheology, particularly the role of a dynamic interfacial tension. The formation of a droplet implies the creation of new interface, to which emulsifiers will adsorb. If the expansion rate of the droplet interface is large, the emulsifier transport will not be able to keep up and the dynamic interfacial tension that determines droplet growth and detachment will be close to the value for a clean interface. By contrast, if the interfacial expansion rate is small the dynamic interfacial tension will be close to the equilibrium value. Schröder *et al.* [58] were among the first to consider these aspects, showing that rapidly adsorbing small-molecule emulsifiers produce smaller droplets than more slowly adsorbing macromolecules. Rayner *et al.* [67] and Van der Graaf *et al.* [27, 68] have considered this further. De Luca *et al.* [63] have discussed the incorporation of the dynamic interfacial tension into the torque- and force-balance models of Peng and Williams [24], which then require numerical solution.

7.2.2
PME

Premix membrane emulsification (also known as dead-end ME) was introduced by Suzuki *et al.* [37, 38] as mentioned previously, and has since been studied by several authors. In the context of understanding the process at the pore level one can state that the modeling of PME has not yet been developed in much detail. One reason is the fact that experimental observations at the pore scale are lacking, since the droplet break-up behavior within the membrane cannot be observed with methods like videomicroscopy. Van der Zwan *et al.* [29] have recently tried to bridge this gap by monitoring droplet behavior in thin microengineered model structures between glass plates using video-microscopy, and they observed quite complex behavior. First, they noted that an accumulation of droplets within the model membrane occurred in all cases, probably because the transport of droplets through the membrane is hindered more by the internal structure (e.g., bending and diameter variations of the channels) than the flow of the continuous phase. The behavior of individual droplets is thus greatly affected by the presence and behavior of neighboring droplets. Moreover, droplets can temporarily (or sometimes permanently) block certain channels. This causes rather erratic changes in flow throughout the structure. Van der Zwan *et al.* [29] were able to distinguish three modes of droplet break-up, that is, break-up due to localized shear forces, break-up due to interfacial tension effects and break-up due to steric hindrance between droplets. Moreover, they observed that break-up also occurs outside the membrane, within the layer of accumulated droplets at the upstream side. Modeling of these phenomena to a similar level of detail as for XME is clearly very complex, and has not been attempted up to now. In subsequent work Van der Zwan *et al.* [69] used a bed of small beads as a model PME membrane, and found that a correlation between droplet size and energy input per unit volume can be established.

7.2.3
MCE

Droplet generation by MCE has been investigated in detail using high-speed video-microscopy, CFD, and LB simulations [25, 26, 30, 31]. Screenshots portraying droplet generation via an MC and a terrace are presented in Figure 7.3.

The dispersed phase that passes through the MC gradually expands on the terrace (Figures 7.3a and b), and then the dispersed phase that passes through the terrace outlet starts to expand into a well. In the initial stage of this detachment process, the Laplace pressure of the dispersed phase on the terrace ($\delta P_{\text{Lap,terrace}}$) is lower than that in the well ($\delta P_{\text{Lap,well}}$). $\delta P_{\text{Lap,well}}$ gradually decreases with the increasing size of the expanding dispersed phase in the well, whereas $\delta P_{\text{Lap,terrace}}$ is almost constant during this stage. Afterwards, $\delta P_{\text{Lap,terrace}}$ becomes significantly higher than $\delta P_{\text{Lap,well}}$, causing rapid flow of the dispersed phase into the well. In this case, the dispersed phase on the terrace shrinks rapidly until a neck is formed on the terrace (Figures 7.3c–e). This behavior is driven by interfacial tension [25]. When the
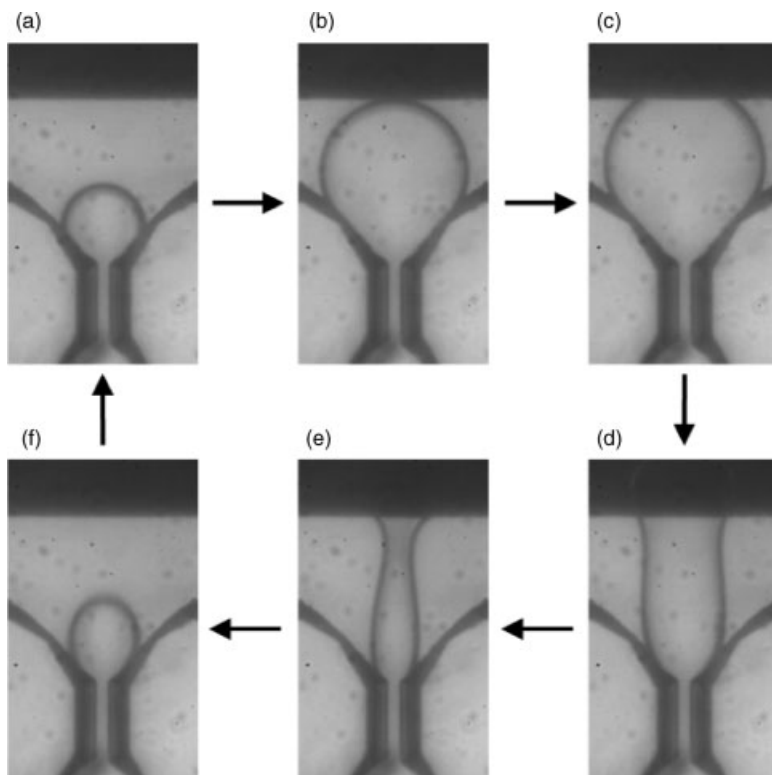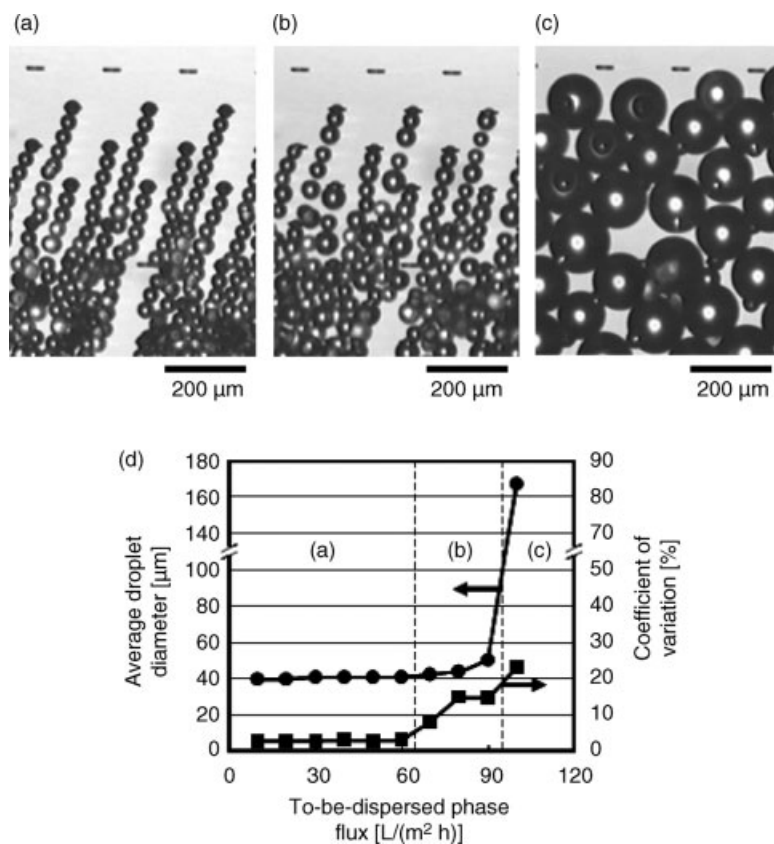

Figure 7.3 Screenshots of droplet generation for MCE. Refined soybean oil was used as the dispersed phase, and Milli-Q water containing 1 wt% sodium dodecyl surface (SDS), as the continuous phase.

dispersed-phase flux at the neck exceeds that in front of the neck [31], the neck instantaneously pinches off and a droplet is generated (Figures 7.3e and f). During this process, the dispersed-phase pressure at the neck becomes remarkably higher than that on the terrace and in the well [26]. Uniform droplets are periodically generated by spontaneous transformation of the dispersed phase that passes through the MC in the absence of a cross-flowing continuous phase. Given the dispersed-phase flow in a 10-mm MC, the interfacial tension is by several orders of magnitude greater than the gravitational force, inertial force, and viscous force [70]. The effect of interfacial tension becomes more dominant as the MC becomes smaller, which is advantageous for producing many food emulsions. Although key points of the MCE process have been clarified in the literature, further work should be conducted to obtain a complete understanding of the droplet-generation process.

In MCE, the droplet size is determined primarily by the geometry of the MC array and can be tuned by changing the viscosity ratio of the two phases. Sugiura *et al.* [71, 72] studied the effect of the MC and terrace dimensions on droplet size. The parameters most affecting the resultant droplet diameter were the MC (and terrace) depth and the terrace length [71]. Analytical models for predicting the droplet size for MCE have been proposed by van Dijke *et al.* [31] and Sugiura *et al.* [71]. These prediction models consider the effects of the MC and terrace structures, the dispersed-phase pressure, and the interfacial tension and contact angle, but do not include the viscosity effect. The MC width and length, which hardly affect the droplet size, are the parameters affecting the droplet productivity per MC [72]. Using long, square MCs leads to generation of uniform droplets of a specific size at high productivity due to the great pressure drop of the dispersed phase in the MC.

The droplet size is not sensitive to the flow velocity of the dispersed phase inside the MC or to the applied pressure of the dispersed phase below a critical value, unlike XME and RME. This robust feature is advantageous for the practical production of monodisperse emulsions. Sugiura *et al.* [73] investigated the flow state of the dispersed phase during MCE and reported that the character of droplet generation from MCs is determined by a dimensionless number called the capillary number (Ca), defined as the ratio of the viscous force to the interfacial tension. The reported critical Ca was approximately 0.02, indicating that the interfacial tension basically dominates the flow state of the dispersed phase during droplet generation. Below the critical Ca, the droplet size was independent of Ca. In contrast, above the critical Ca, the droplet size increased sharply with increasing Ca. The effect of viscous force may become significant in this Ca range. It is also worth noting that the size and size distribution of the monodisperse emulsions produced by MCE is not sensitive to the flow rate of the dispersed phase below the critical value (Figure 7.4) [55].

Monodisperse emulsions can be stably produced by MCE when the continuous phase preferentially wets the surface of an MCE chip [51, 55, 74, 75]. The electrostatic interaction between the chip surface and emulsifier molecules also critically affects droplet generation from MCs. Uniform droplets can be generated when the MCE chip used has a nonattractive interaction with emulsifier molecules. It is important to keep the charge of the chip surface and emulsifier used in mind during MCE as well as ME.

Figure 7.4 Effect of the dispersed-phase flow rate on the size and size distribution of the produced O/W emulsions [55]. Refined soybean oil was used as the dispersed phase, and Milli-Q water containing 1 wt% sodium dodecyl surface (SDS), as the continuous phase.

7.3
Production of Structured Systems for Food Applications

7.3.1
O/W Emulsions

7.3.1.1 Membrane Emulsification

O/W emulsion is important on the formulation of many food products. Food emulsions normally require droplet size in the range of 0.1 and 30 µm, mayonnaise, salad dressing, cream liqueurs, and ice cream, milk and dairy drinks.

An overview on the production of single and multiple emulsions, gel microbeads, solid lipid microparticles, protein microspheres by ME was reported by Vladislavljevic and Williams [7, 76]). You *et al.* [77] have produced gel particles as calcium alginate using ME, where a microporous glass membrane of 2.9 µm average pore diameter was

used to produce calcium alginate microspheres with 4 µm mean diameter. Another example is Liu *et al.*'s [78] work, where they used metallic membrane with pore diameter raging from 2.9 to 5.2 µm to produce uniform calcium alginate spherical beads with mean diameter of 50 µm. Both groups observed that transmembrane pressure is one of the most important process parameters to determine final particle size and its size distribution. Solid lipid particles were produced by ME, as shown by D'oria *et al.* [79]. Mean particles size from 50 to 750 nm could be reached at disperse phase flow rates up to $0.84\,m^3\,m^{-2}\,h^{-1}$. Fouling limited the production rate when membranes with small pore diameter (0.2 and 0.4 µm) were used.

As a food formulation Gijsbertsen-Abrahamse *et al.* [37] have computationally simulated a culinary cream containing 30% fat using three different type of membranes (SPG, ceramic and microsieve) with 0.2 µm pore diameter. A microsieve membrane provided the best performance for an industrial scale production due to its lowest porosity ($\varepsilon = 0.01$) compared to SPG ($\varepsilon = 0.6$) and ceramic ($\varepsilon = 0.35$) membranes.

7.3.1.2 Microchannel Emulsification

Much of the MCE literature has discussed the production of O/W emulsions consisting of food-grade substances. The surfaces of MC arrays as well as the membrane surfaces must remain sufficiently hydrophilic during MCE. Prior to first usage, MC emulsification chips made of single-crystal silicon are subjected to plasma oxidation in order to grow a hydrophilic silicon dioxide layer on the surface of the MC arrays [55].

Vegetable oils (refined soybean oil and high oleic sunflower oil) and medium-chain triglyceride (MCT) have been used as the dispersed phase for producing monodisperse O/W emulsions by MCE [51, 80]. Tan *et al.* [81] also demonstrated that monodisperse O/W emulsions are produced when refined palm olein is used after removing monoglycerides and diglycerides. Thus, it is necessary to keep in mind that the hydrophobicity of the dispersed oil phase is a critical parameter affecting the generation of oil droplets in MCE. Since food-grade oils are generally viscous liquids at room temperature, the ratio of the dispersed-phase viscosity to the continuous phase viscosity is usually high unless the continuous water phase contains a considerable amount of thickeners. This high viscosity ratio has the merit that droplet generation is not sensitive to operating conditions. The first generation of MCE chips, called grooved MC array chips, have a throughput of vegetable oil droplets of less than $1\,L\,m^{-2}\,h^{-1}$. Kobayashi *et al.* [54] developed straight-through MC array chips as high-throughput MCE chips, realizing the generation of uniform vegetable oil droplets at a high dispersed-phase flux of up to $65\,L\,m^{-2}\,h^{-1}$. In MCE, monodisperse O/W emulsions can also be produced using chemical oils (e.g., alkane oils and silicone oils) with a wide viscosity range of 1 mPa s to 10^3 mPa s and a continuous water phase with a viscosity of 1 mPa s [82, 83]. Droplet production per MCE chip tends to increase as the dispersed-phase viscosity decreases, indicating that MCE at an elevated temperature can increase the production of vegetable-oil droplets.

The effect of food-grade emulsifiers on MCE has been reported several times in the literature. Several nonionic emulsifiers (Tween® 20, Tween® 80, pentaglycerin

monolaurate, and sucrose monolaurate) have been demonstrated to be appropriate for stably generating uniform droplets by MCE [75, 84, 85]. Although uniform vegetable oil droplets were generated from an MC array in the absence of emulsifiers, the generated droplets were unstable, as was expected [84]. The results reported in the literature suggest that hydrophilic nonionic emulsifiers with a hydrophile–lipophile balance (HLB) exceeding 10 must be used in order to stably produce monodisperse O/W emulsions by MCE. Tong *et al.* [86] investigated the production of O/W emulsions stabilized by phospholipids, demonstrating that uniform oil droplets were generated using a continuous water phase containing anionic lyzophosphatidylcholine (LPC). Interestingly, droplet generation was made more stable by using lecithin in the dispersed phase and LPC in the continuous phase. The effect of proteins as an emulsifier on MCE was also investigated by Saito *et al.* [87]. Droplet-generation behavior (Figure 7.5) was found to be highly relevant to protein solution properties, such as the isoectronic point (pI), contact angle, and interfacial tension. When the pH of the continuous water phase was close to 7, MCE generated uniform vegetable oil droplets stabilized by bovine serum albumin (BSA), b-lactoglobulin, soybean flour, or whey protein, which have a low pI, a high contact angle of an oil droplet, and/or low interfacial tension. In contrast, no droplets were generated for a continuous water phase containing lysozyme (pI: 10.5–11.0) or egg-white protein. It is also important to control the pH of the continuous water phase during MCE, since
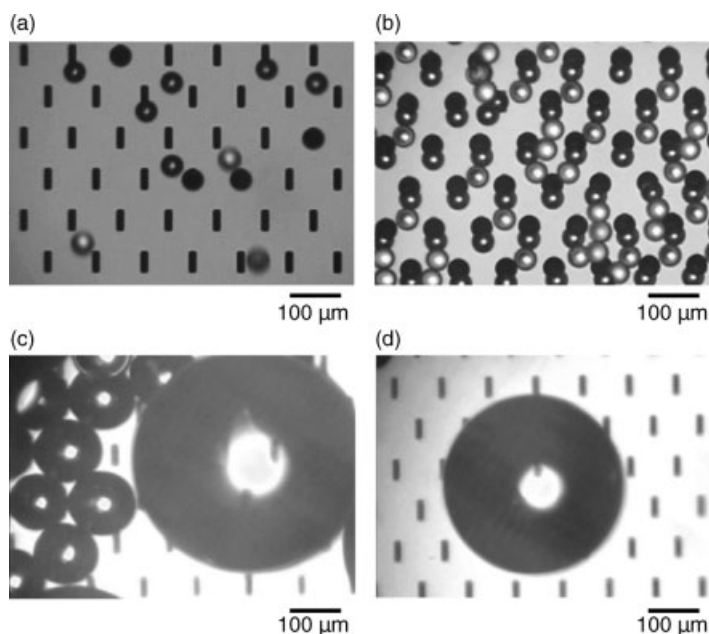

Figure 7.5 Generation of soybean oil-in-water emulsion droplets stabilized by proteins from MCs [87]. (a) and (b) Generation of uniform droplets. (c) Unstable generation of nonuniform droplets. (d) Wetting of the dispersed phase on the chip surface.

the charge of the protein molecules reverses close to pI. As described in Section 7.2, the charge of an emulsifier greatly affects its interaction with the negatively charged surface of an MC array as well as the droplet generation. Uniform droplets stabilized by negatively charged BSA molecules were generated at pH values over pI at 4.7–4.8, whereas the dispersed phase covered by positively charged BSA molecules wetted on the chip surface at pH values below pI.

Food-grade O/W emulsions produced by MCE have been applied to produce monodisperse microparticles and microcapsules. Sugiura *et al.* [88] obtained dispersions of monodisperse solid lipid microparticles by cooling uniform droplets of melted oils (tripalmitin and hydrogenated fish oil) generated using MCE. Kobayashi *et al.* [89] produced dispersions of tripalmitin microspheres by MCE and subsequent solvent evaporation. The MCE in this work produced monodisperse O/W emulsions consisting of hexane, which was chosen as a solvent. Although dichloromethane is commonly used for solvent evaporation, this solvent is not available for food applications. The hexane in the oil droplets successfully transferred to the continuous water phase during solvent evaporation at atmospheric pressure and room temperature, considerably reducing the droplet size (Figure 7.6). Nakagawa *et al.* [90] produced dispersions of monodisperse gelatin/acacia complex coacervate microcapsules by MCE and subsequent coacervation. The single-core microcapsules were prepared using uniform vegetable oil droplets stabilized by appropriate types of gelatin. Chuah *et al.* [91] formulated monodisperse O/W emulsions stabilized by a layer of an electrolyte complex of negatively charged modified lecithin and positively charged chitosan (Figure 7.7). Uniform vegetable oil droplets stabilized by modified lecithin were initially generated by MCE. Adding a sufficient amount of chitosan to the preceding O/W emulsions yielded positively charged oil droplets, with higher stability against heating (particularly at 70–90 °C) and long-term storage at pH 3 than oil droplets stabilized solely by modified lecithin. The above-mentioned monodisperse microparticles and microcapsules produced by this process are promising for food applications, although their production scale is currently less than 1 g h^{-1}. Their throughput must be scaled up for practical-scale production.
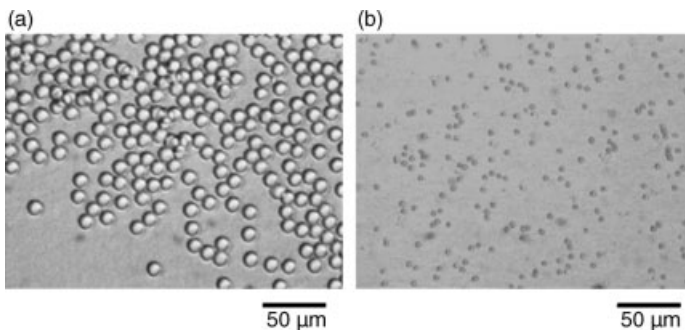
Figure 7.6 Size reduction of uniform oil droplets by solvent evaporation [89]. (a) Optical micrograph of uniform hexane oil droplets containing tripalmitin produced by MCE. (b) Optical micrograph of uniform tripalmitin microspheres after solvent evaporation.
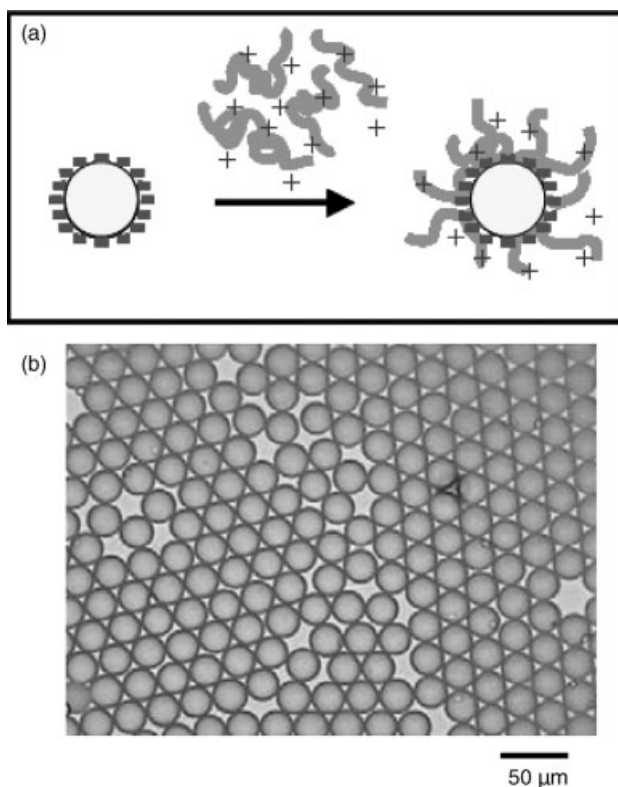
Figure 7.7 (a) Schematic drawing of the formation process of electrostatic complex on the droplet surface. (b) Optical micrograph of uniform soybean oil droplets stabilized by a thin layer of electrostatic complex of modified lecithin and chitosan [91].

7.3.2
W/O Emulsions

7.3.2.1 Membrane Emulsification
Most of the ME/MC literature concerns oil-in-water (O/W) emulsions, however, the production of water-in-oil (W/O) emulsions has also been discussed [16].

The basic principles set out in the previous chapters apply to both cases, but in practical terms the preparation of W/O emulsions with ME (both XME and PME) differs in two important aspects from the O/W case. First, a hydrophobic membrane surface has to be provided and maintained. Secondly the viscosity ratio of dispersed and continuous phase can be quite different. The latter may not be very significant when low-viscosity hydrocarbons and water are involved (viscosity ratio not far from unity), but for food emulsions based on vegetable oil ($\sim$50–60 mPa s at room temperature) the viscosity ratio can differ by up to two orders of magnitude between an O/W and W/O emulsion made from the same materials, unless the water phase is thickened considerably.

Providing a hydrophobic surface can be done by modification of the usual hydrophilic membranes like Shirasu-porous-glass (SPG) membranes. The papers by Cheng *et al.* [92, 93] provide recent examples of this approach, in which a silane coupler or a silicone resin was used to render the surface of SPG membranes hydrophobic. Also, silicon nitride microsieves and perforated steel plates have been made hydrophobic via chemical surface treatment [94, 95]. Katoh *et al.* [15] have simply soaked SPG membranes thoroughly in the oil phase prior to the ME preparation of W/O emulsions. Sotoyama *et al.* [96] have also used this approach, and suggested that the added emulsifier in the oil (in their case poly-glycerin polyricinolate, PGPR) adsorbs to the silanol groups on the glass surface creating a hydrophobic base. This soaking procedure is potentially an attractive option for food applications as there is no risk of gradual wear of adsorbed chemicals from the membrane. However, more work will be needed to determine how strong the effect is for a given oil + emulsifier and how long the effect persists. Another option for getting the right wetting behavior is to use membranes made of a hydrophobic material like polypropylene [97] or polytetrafluoroethylene [98]. The latter authors investigated both kerosene and corn oil (with emulsifiers) as the oil phase, and found that preparation of a corn-oil-based W/O emulsion was not possible at moderate transmembrane pressure. This was attributed to the wetting behavior of the PTFE, which appeared to be nonwetting for the corn oil. It is noteworthy that Vladislavljevic *et al.* [97] and Yamazaki *et al.* [98] have also used presoaking with the continuous oil phase, and that the former authors found a significant effect on droplet size and dispersed phase flux at given transmembrane pressure.

7.3.2.2 Microchannel Emulsification

The production characteristics of W/O emulsions using MCE have been reported several times in the literature. A prerequisite for producing monodisperse O/W emulsions by MCE is to keep the surface of MC arrays hydrophobic, similar to ME. Hydrophobic treatment of silicon MCE chips is conducted by modifying their hydrophilic surface using a silane-coupler reagent [51, 99]. Liu *et al.* [100] and Kobayashi *et al.* [101] have developed MCE chips made of a naturally hydrophobic polymer (poly(methyl methacrylate), PMMA). PMMA grooved MC arrays were fabricated by injection molding [100], and PMMA straight-through MC arrays were fabricated as part of the (Lithographie, Galvanoformung, Abformung (LIGA) pro-cess [102]. MCE chips made of PMMA as well as membranes made of hydrophobic materials do not require any chemical surface modification, which is advantageous for food applications. However, polymeric MCE chips are not strong against organic solvents frequently used as the continuous oil phase.

In MCE, W/O emulsions have generally been produced using alkane oils with low and medium carbon numbers as the continuous phase due to their low viscosity. Only two studies have reported the production of water-in-triglyceride emulsions using MCE [99, 103]. Uniform water droplets could be generated in the absence of thickeners in triglyceride oils (MCT oil, soybean oil, or triolein oil) as the continuous phase via MC arrays (Figure 7.8). As mentioned earlier, the viscosity ratio of the dispersed water phase to the continuous triglyceride-oil phase decreases by two or
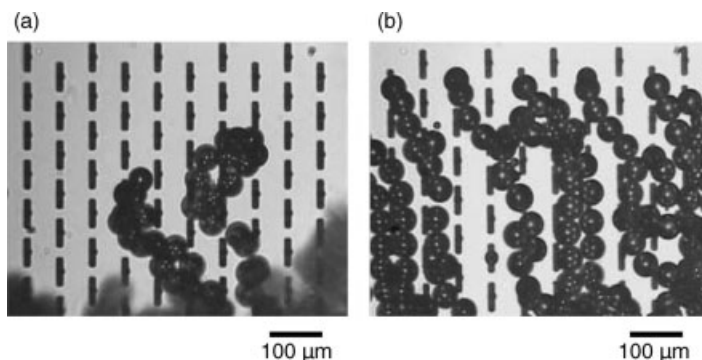
Figure 7.8 Production of monodisperse water-in-triglyceride oil emulsions stabilized by a hydrophobic emulsifier using MCE. The oils used were MCT oil (a) and refined soybean oil (b). The osmotic pressure of the dispersed phase was 4.2 MPa [99].

three orders of magnitude compared to O/W emulsions made of the same two liquids. Optical microscopy during MCE suggests that droplet generation using water-in-triglyceride oil systems is less stable and more sensitive than water-in-alkane oil systems, a finding that could be attributable to the very low viscosity ratio of the former systems. Moreover, the use of the viscous continuous phase results in a quite low droplet-generation rate per MC, which can be somewhat increased by operating the MCE at an elevated temperature.

For the effect of the dispersed water phase, its osmotic pressure is a critical parameter affecting droplet-generation behavior. Kobayashi *et al.* [99] clearly demonstrated that monodisperse W/O emulsions were stably generated at osmotic pressures above a critical value and that nonuniform water droplets are unstably generated below the critical osmotic pressure (Figure 7.9). At low osmotic pressures, an aggregated layer driven by spontaneous emulsification was formed around the expanding dispersed phase and the generated droplets (Figure 7.9), which may prevent smooth movement of the water/oil interface inside an MC array. Food-grade nonionic emulsifiers have been primarily used to produce W/O emulsions in MCE. Sorbitan fatty acid esters were successfully used to produce monodisperse W/O emulsions [74]. Sugiura *et al.* [103] screened polyglycerin fatty acid esters and polyglycerin condensed ricinoleic acid esters suitable for producing monodisperse W/O emulsions. Polyglycerin condensed ricinoleic esters with a very low HLB value (<1) were found to be particularly suitable for stably generating uniform water droplets. In contrast, the use of soybean and egg-yolk lecithins resulted in unstable generation of water droplets and their immediate coalescence.

Until now, monodisperse gel microbeads and giant vesicles have been obtained using uniform water droplets produced by MCE as templates. Kawakatsu *et al.* [104] produced monodisperse albumin gel microbeads by denaturing droplets of albumin aqueous solution dispersed in a continuous oil phase. Iwamoto *et al.* [105] obtained monodisperse gelatin gel microbeads by cooling droplets of gelatin aqueous solution produced by MCE at an elevated temperature. The particle size hardly changed during gelation of the droplets containing albumin, whereas a significant decrease in
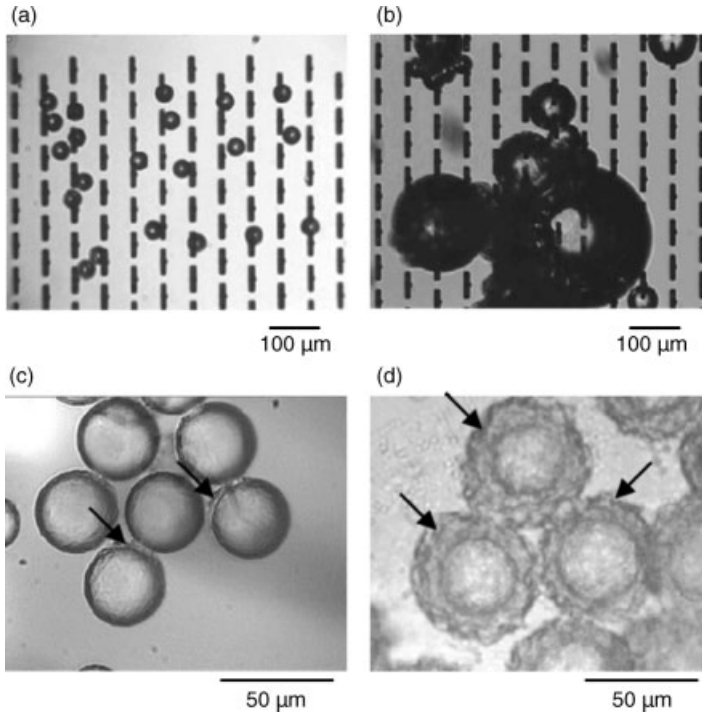
Figure 7.9 (a) and (b) Effect of the osmotic pressure of the dispersed phase on the generation of W/O emulsion droplets from MCs. (a) Generation of uniform aqueous droplets at an osmotic pressure of 4.2 MPa. (b) Unstable generation of nonuniform Milli-Q water droplets. (c) and (d) Formation of aggregates around the generated Milli-Q water droplets. Optical micrographs of the resultant water droplets just after generation (c), after 20 min (d).

particle size occurred during gelation of the droplets containing gelatin. Monodisperse gel microbeads are considered to be promising microcarriers for functional food ingredients; however, more work has to be done to precisely control their particle size and to produce monodisperse gel microbeads encapsulating functional food ingredients. Monodisperse giant vesicles have also been obtained by the "lipid-coated ice droplet hydration method" using aqueous droplets dispersed in the continuous phase of a hexane solution generated by MCE (Figure 7.10) [106, 107]. The monodisperse giant vesicles consist of food-grade substances, but phosphatidylcholine used as an emulsifier is very expensive; therefore, they would be promising for pharmaceutical applications.

7.3.3
W/O/W Emulsions

7.3.3.1 Membrane Emulsification
The first work on the production of multiple emulsions was published in 1923 [108]. Multiple emulsions are complex structures with special properties as carrier systems,
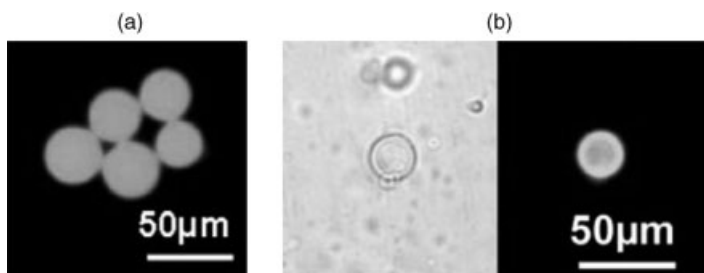
Figure 7.10   (a) Optical micrograph of W/O emulsion droplets generated by MCE. (b) Images of a giant vesicle observed by bright-field light microscopy (left) and by fluorescence microscopy (right) [107].

and have been recently used in the manufacturing of low energy density food products. Muschiolik *et al.* [49, 109] have reported the production of multiple emulsions (W/O/W) by cross-flow and rotating membrane emulsification, single and double T-junction microchannel, and glass capillary (coaxial jet). More recent developments on the production of double emulsions using microfluidic devices, including membrane and microchannel emulsification were published by Vladislavljević and Williams [76] and others as cited in Section 7.3.2.2.

Stability of multiple emulsions can be influenced by different factors as Laplace and osmotic pressures between internal and external phases, interaction between emulsifiers (low and high HLB), also between thickener and high HLB emulsifier, and viscosity of both phases [110, 111]. Membrane emulsification is a suitable process to produce multiple emulsions as process conditions are favorable due to low shear rates during processing. Their physical stability against Ostwald ripening, consequently long-term shelf life, depends on the balance between Laplace and osmotic pressures as previously mentioned. Such balance can be reached by adding salt to W_1 (inner aqueous phase). A viscosity ratio of 1 between W_2 (outer aqueous phase) and W_1/O is preferable for the production of successful multiple emulsions. Thickeners, such as guar gum, xanthan gum, gelatin, maltodextrin (DE > 10), hydroxyethylcellulose. For the production of W_1/O (dispersed phase), PGPG (polyglycerol ester of ricinoleic, HLB = 4) and modified lecithin have been used for food applications, and nonfood grade cetyl dimethicone copolyol, PEG-30 dipolyhydroxystearate (block copolymer).

W/O/W emulsions are promising structured systems for applications in the food industry for low-fat food formulations [112], and also delivery systems of (bio)active molecules. Kanouni *et al.* [110] has suggested the use of W/O/W emulsions on the formulation of sauce, mayonnaise, where a less oily taste may be reached. Another advantage is the formulation of low fat food products. Skin creams may also provide a different feeling after rubbing on skin.

As an example, food-grade W/O/W emulsions were produce by dead-end membrane emulsification with droplet size of 100 μm [4]. An SPG membrane was used for the production of narrow droplet-size distribution with the smallest span of about 0.28 at high flow rate. Several passes allowed very narrow droplet-size distribution.

W/O/W emulsions containing whey protein isolate in the water internal droplets were produce using the same process. Gelation of internal water droplets by whey protein provided the smallest particle size and narrowest particle-size distribution [113].

7.3.3.2 Microchannel Emulsification

Production of W/O/W emulsions using MCE has been investigated in a few studies. The W/O/W emulsions were produced by two-step emulsification processes. As a first-step emulsification, W/O emulsions was prepared by homogenization [114, 115] or microfluidization [116]. Homogenization yielded W/O emulsions with an average droplet size on the order of several micrometers to several tens of micrometers. In contrast, microfluidization enabled the preparation of fine W/O emulsions with an average droplet size as small as 150 nm. In second-step emulsification (MCE), oil droplets containing smaller water droplets were generated by injecting a W/O emulsion into a continuous external water phase through MCs. During MCE, the hydrophilic surface of the silicon MCE chip must be maintained in order to produce monodisperse W/O/W emulsions. Water-in-triglyceride oil emulsions (soybean oil, triolein, or MCT-oil) have been successfully used to produce monodisperse W/O/W emulsions by MCE [114–116]. The monodisperse W/O/W emulsions were stabilized by two food-grade emulsifiers: a hydrophobic emulsifier dissolved in the medium oil phase and a hydrophilic emulsifier dissolved in the external water phase. In addition, the osmotic pressure of the internal and external water phases must be appropriately controlled in order to obtain stable W/O/W emulsions as well as feed W/O emulsions. Kobayashi *et al.* [116] demonstrated that the volume fraction of fine water droplets dispersed in uniform oil droplets can be controlled and increased up to 30% (Figure 7.11). It is necessary to mention that no leakage of the internal water droplets was observed during MCE. Only one study has reported the production of dispersions based on the produced monodisperse W/O/W emulsions. Kawakatsu *et al.* [114] obtained food-grade S/O/W emulsions by electrolyte-induced gelation of the internal phase of a pectin aqueous solution. Currently, one can find a much greater number of studies that discuss the production of W/O/W emulsions using ME as the first-step and/or second-step emulsification (see Section 7.3.3.1). In particular, information about two-step emulsification processes using SPG membranes would be directly applicable to the production of W/O/W emulsions using MCE.
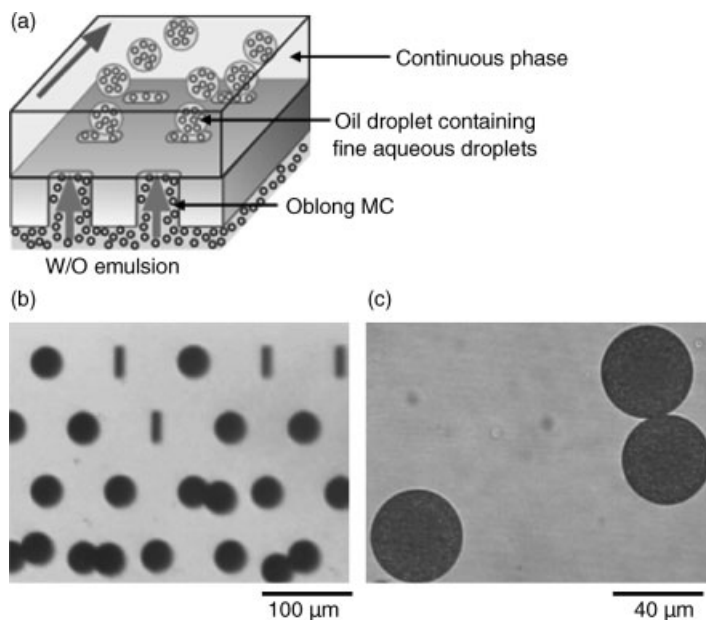
7.4
Encapsulation of Active Molecules

7.4.1
Membrane Emulsification

Membrane and microchannel emulsification are gently technologies to encapsulate sensitive compounds into single and multiple emulsions, as well as microcapsules [7], due to its low shear rate during processing. Multiple emulsions are also

Figure 7.11 (a) Schematic drawing of the production of a W/O/W emulsion by MCE. Size (b) Optical micrograph of the generation of uniform soybean oil droplets containing aqueous droplets from MCs. (c) Optical micrograph of the generated oil droplets containing many submicrometer aqueous droplets. The volume fraction of the internal water phase in the oil droplets was 30% [116].

potential matrixes to encapsulate active molecules for inumerous applications in food, cosmetic, and pharma industries [76, 117, 118]. They have been used in the encapsulation of compounds as drugs [119], vitamins, retinyl palmitate, carotenoids, polyphenols [120], flavors, ions Mg^{2+} [121], and antimicrobials [8, 122]. These carrier systems may protect sensitive compounds against chemical, and enzymatic degradations; and mask undesirable taste.

Literature has shown a successful incorporation of microorganisms into microcapsules by membrane emulsification. Zhou *et al.* [123] studied the encapsulation of bacterial cells into uniform-sized agarose microcapsules by membrane emulsification. Cell growth could be observed after 14 days of incubation time and it showed that this mild process was able to preserve cell viability. In another research work, uniform droplets and microcapsules containing *Lactobacillus casei* were also produced by ME [124] for further application in dairy products.

Monodisperse W/O chitosan emulsion as insulin carrier systems was prepared by membrane emulsification and followed by cross-linking using tripolyphosphate (TPP) and glutaraldehyde for two steps of particle solidification [125]. Uniform-sized microspheres were able to keep insulin activity and provide high encapsulation efficiency.

Ribeiro *et al.* [42] investigated the encapsulation of astaxanthin, a carotenoid, in O/W emulsion by dead-end membrane emulsification. For the production of smaller

droplet size and narrower droplet-size distribution, three passes through the membrane were used. A strong fouling could be observed due to the protein used as the emulsifier.

7.4.2
Microchannel Emulsification

Droplet generation for MCE is a very mild process driven by spontaneous transformation of the dispersed phase that passes through the MCs [103]. The energy input for MCE is also very low (e.g., 10^3–10^4 J m^{-3}), indicating that temperature elevation during emulsification can be neglected [103]. These features are attractive for preventing the degradation of shear- and heat-sensitive active molecules. Monodisperse O/W emulsions consisting of hydrophobic active molecules using MCE have been recently produced by Neves *et al.* [85, 126]. Neves *et al.* [85] first discussed the generation of soybean oil droplets containing beta-carotene of gamma-oryzanol from MCs. Uniform oil droplets containing gamma-oryzanol were generated in a continuous phase containing a food-grade hydrophilic emulsifier at room temperature. For beta-carotene, MCE was conducted at an elevated temperature to prevent recrystallization of beta-carotene dissolved in the soybean oil, resulting in uniform oil droplets. Neves *et al.* [126] also generated droplets of refined palm oil rich in beta-carotene and fish oil droplets or a mixture of palm oil and fish oil rich in polyunsaturated fatty acids. Droplet production per MCE chip was almost independent of the concentration of the active molecules [126].

Sugiura *et al.* [106, 115] discussed the entrapment yield of model fluorescent molecules (calcein) in a W/O/W emulsion and giant vesicles obtained using MCE. Hydrophilic calcein was added in the internal water phase before producing the W/O emulsions. The entrapment yield in the W/O/W emulsion was very high (91%), which is considered to be attributable to the very mild droplet-generation process via MC arrays [113]. Giant vesicles obtained by Sugiura *et al.* [106] had the highest entrapment yield of approximately 35%, comparable to the reverse-phase evaporation method, and was significantly higher than most other giant-vesicle formation processes. In this case, 67% of the calcein leaked out from the internal water phase, mainly during the hydration step. A further modification of the hydration process must be undertaken to achieve higher entrapment yields.

7.5
Assessment of the Potential Benefits of Membrane Emulsification in Foods

The potential benefits of ME have been discussed by many authors, for example, Joscelyne and Trägård [3], Charcosset *et al.* [34] and quite recently Charcosset [9]. In fact, low shear, low power input and narrow droplet-size distribution (compared to conventional emulsification) are mentioned as benefits in the introduction of all papers on ME, but this is rarely discussed in more detail from a food-industry point of view. In this section we will try to fill this gap to some extent by taking a food product

developer perspective and assess what mild processing and a narrow droplet-size distribution (DSD) can actually be expected to contribute to the consumer-perceived properties of a food product. In our view this is less evident than most academic ME literature suggests, and realizing this should help to focus the efforts on the industrialization of ME for foods applications.

7.5.1
DSD and Product Stability

A narrow droplet-size distribution is frequently claimed to enhance product stability during shelf life, which may be divided into physical, chemical and microbiological stability.

7.5.1.1 Physical Stability

Physical stability typically refers to two aspects: (1) changes in the DSD via coalescence or Ostwald ripening, and (2) creaming or settling of the droplet phase. In principle, the width of the DSD can indeed affect these processes. The difference in Laplace pressure between droplets of different size is the driving force for Ostwald ripening, so this process will be slow if the DSD is narrow. Furthermore, a distribution in droplet size implies a distribution in creaming/settling velocity. This promotes the occurrence of droplet collisions, which may enhance coalescence if the droplets are not well stabilized. Also, the overall creaming/settling rate can be enhanced, because larger droplets tend to drag smaller ones along in their slipstream [127].

While this argumentation is valid in principle, its practical importance depends on the food emulsion considered. In many food products creaming/settling is prevented anyway because the continuous phase is structured by fat crystals or gelling agents (e.g., margarine, dressings), because the volume fraction is so high that the closest packing is obtained (mayonnaise), or because the droplet phase is clustered into a space-filling network (certain creams). In fully liquid products that require long-term stability, the droplet size as such can be so small that Brownian motion counteracts creaming (cream liqueur). In other semiliquid emulsions the phase separation is simply accepted. In those cases the droplets are well stabilized against coalescence and the consumer is requested to shake the bottle before use.

For most oil-in-water (O/W) products, the timescale for Ostwald ripening exceeds the product shelf life. This is due to a combination of low solubility of triglyceride oils in water and mass transfer limitations presented by protein layers at the interface. In semisolid W/O emulsions like margarines a fat crystal shell around the droplets provides a mass transfer limitation as well as a mechanical restriction on droplet size changes. In more liquid-like W/O emulsions (e.g., pourable margarine) an osmotic stabilization against Ostwald ripening can be provided by salt in the water phase [128], which is often there for taste reasons anyway.

Summarizing, practical cases where a narrow DSD could help to solve an urgent problem with the physical stability of a food emulsion are not readily apparent.

7.5.1.2 Chemical Stability

Lipid oxidation and the consequent production of off-flavors is a general problem in products based on triglyceride oils. For O/W emulsions, the DSD at given volume fraction can play a role here in principle, as it determines the interfacial area between the oil and the water. In a review of lipid oxidation in O/W emulsions, McClements and Decker [129] pointed out that only a limited number of studies have been done into the effect of droplet size on oxidation. Some indeed corroborate the expectation that oxidation increases with decreasing droplet size at given volume fraction, due to the increase in interfacial area. One study found no effect. McClements and Decker [129] suggested that the presence of catalytic species with a preference for the interface could explain this observation. If all available catalyst species reside at the interface anyway, the interfacial area becomes unimportant. In any case reducing the total interfacial area by narrowing the DSD has only limited potential. Assuming a lognormal size distribution and typical parameters for conventionally produced emulsions we have estimated that a perfectly monodisperse emulsion of the same volume fraction would only have a 30% smaller total interface.

7.5.1.3 Microbiological

Micro-organisms can grow in the water phase of the emulsion, which implies that droplet size is of primary important in W/O emulsions. Water droplets can be made small enough to suppress the growth of micro-organisms due to insufficient amount of nutrient per drop and to space limitation within a small drop [130]. Obviously, the maximum droplet size is the key parameter here. The width of the DSD does not play a direct role.

7.5.2
DSD and Product Rheology

The rheology of dispersions and emulsions has been the subject of many textbooks and articles, and a full review is well beyond the scope of the present discussion. Rather, we want to focus on a limited number of references in which the role of polydispersity of the dispersed phase is considered.

The most relevant rheological parameters for food-type emulsions are:

- viscosity;
- the linear viscoelasticity parameters G' and G'';
- the yield stress.

All four parameters depend on the DSD, although in many food emulsions a significant (if not dominant) contribution also comes from structure in the continuous phase. This will not be considered explicitly here.

Often, relations that were originally derived for dispersions of solid particles are used. This is a good approximation when (1) the Laplace pressure is high enough compared to the applied hydrodynamic stress to prevent significant droplet deformation, and (2) the droplet interface behaves quasirigidly with respect to tangential hydrodynamic stress, due to the presence of surface-active molecules or an interfacial

film/skin [131]. However, in practice these relations are also used as a first estimate beyond the range of their strict applicability, because manageable models that take into account droplet deformability as well as interfacial rheology are not readily available.

7.5.2.1 Yield Stress

In many food emulsions that possess a yield stress, this is due to structure in the continuous phase, for example, the fat–crystal network in margarines. An appreciable yield stress due to the dispersed phase is only observed in concentrated emulsions, in which the droplets are closely packed. Mayonnaise (O/W emulsion with 80% oil) is a well-known example. This raises the question at which volume fraction an emulsion becomes close-packed.

For monodisperse solid spheres the maximum packing fraction depends on the type of packing, varying from 0.63 for random packing to 0.74 for a face-centered-cubic (FCC) crystalline lattice. However, both computer simulations and experiments have indicated that the close-packing value for dispersions of monodisperse spheres rarely exceeds the random-packing value, to be denoted henceforth as ϕ_{RCP} [131–135]. Also for $\phi > \phi_{RCP}$ the structure often remains disordered, unless specific measures are taken to make it more regular (e.g., by application of a well-defined flow). Mason *et al.* [131], for instance, have demonstrated via light scattering that the quasimonodisperse emulsions in their experiments were all disordered on a macroscopic length scale, even at volume fractions close to unity.

The consequences of the disordered microstructure of concentrated emulsions for their rheological properties have been discussed in detail by Mason *et al.* [131, 132]. When a stress is applied to a structure with ordered packing, yielding implies a "global topological rearrangement", that is, planes of droplets move in unison. According to computer simulations cited by Mason *et al.* [131], this occurs at strains of the order 0.6 for a 3D ordered lattice. By contrast, a disordered structure allows yielding via local rearrangements of droplets or groups of droplets. This can take place already at much lower strain. Hébraud *et al.* [133] have given an elegant experimental confirmation of this view by probing local rearrangements during the yielding of disordered emulsions via diffusing-wave spectroscopy. The agreement of their calculations and experimental results with the data of Mason *et al.* [131] is also quantitatively good.

Mason *et al.* [131] already conjectured that it is the disordered microstructure of real emulsions rather than their polydispersity that explains the discrepancy between experimental data for polydisperse emulsions and theoretical results for particle packings of monodisperse emulsions. This issue has been considered in more detail by Saint-Jalmes and Durian [135], in a study of polydisperse foams (which are very similar in rheological behavior to concentrated emulsions). These authors found quantitative agreement with the correlation of Mason *et al.* [131], despite the polydispersity of their foams. Also, other rheological parameters were quite similar, which lead Saint-Jalmes and Durian [135] to the conclusion that polydispersity does not play an important role in concentrated systems, as long as it stays moderate and the DSD is unimodal.

7.5.2.2 Elastic Modulus

Mason *et al.* [132] considered the elasticity of concentrated monodispersed emulsions, and found that the elastic shear modulus G' scales as $\phi(\phi - \phi_{RCP})\sigma/R$, where σ is the interfacial tension and R the droplet radius. As for the yield stress, Saint-Jalmes and Durian [135] demonstrated that this correlation also holds for polydisperse foams. Again, their conclusion was that the disordered structure of the foams makes polydispersity of minor importance, and this reasoning can be extended to emulsions.

7.5.2.3 Viscosity

The above rheological properties characterize the resistance of the system to stresses that tend to induce flow. For a flowing emulsion the apparent emulsion viscosity is the most important parameter. The viscosity of a dispersion can be phenomenologically related to the DSD via the well-known Krieger–Dougherty equation, which links the viscosity to the actual and maximum volume fraction of dispersed phase [134, 136]:

$$\mu_{REL} = \frac{\mu}{\mu_C} = \left[1 - \frac{\phi}{\phi_M} \right]^{-[\mu]\phi_M}$$

Here, μ_C is the viscosity of the continuous phase, $[\mu]$ is the so-called "intrinsic viscosity", and ϕ_M is the maximum packing fraction of the droplets. In fact, Barnes [136] suggested that the exponent $-[\mu]\phi_M$ is often close to -2. The relative emulsion viscosity is thus sensitive to the precise value of the maximum packing fraction, which depends on the DSD. Figure 7.12 shows the typical range encountered in food emulsions. The effect becomes significant for volume fractions above about 0.4.

A successful fit of the viscosity to the KD equation, using the maximum packing fraction as a fit parameter, does as such not highlight the physical background of the processes involved. One might ask how particles at volume fractions below the closest packing would "know" what their ϕ_M would be upon increasing the volume fraction. Actually the mechanism of viscosity increase with volume fraction is based on hydrodynamic interactions between the particles, which have a size dependence and thus give a relation to the DSD. Apparently, this can be adequately captured phenomenologically by choosing the ϕ_M that corresponds to the DSD at hand.

7.5.2.4 Formation of Flocculated Networks

The effect of DSD width on aggregation/flocculation has been considered by Bushell and Amal [137] in computer simulations based on diffusion-limited cluster aggregation. They found that the fractal structure and the form of the function that describes the gross shape of the aggregates is unaffected by details of the primary particle-size distribution. Bushell and Amal [137] claimed that their results are consistent with other literature on the effect of polydispersity on aggregation (see their paper for references).
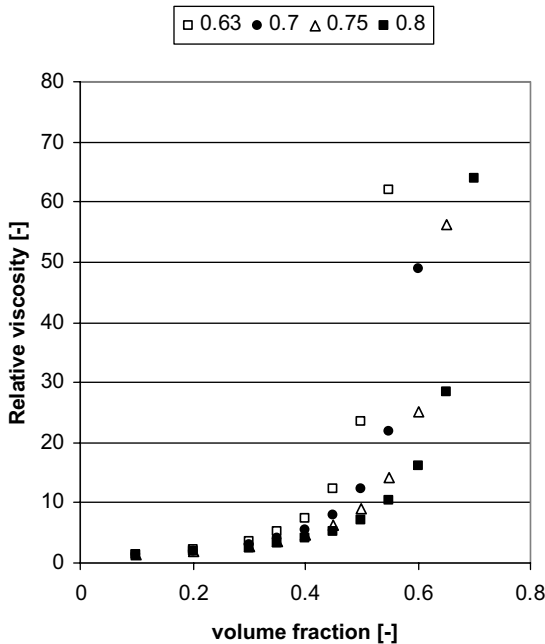
Figure 7.12 Krieger–Dougerthy (KD) relation for different values of the maximum packing fraction.

7.5.3
Product Properties Related to Low-Shear Processing

7.5.3.1 Shear Damage to Ingredients

ME is often claimed to give less deterioration of delicate ingredients. However, the standard macromolecular ingredients like proteins, enzymes, and polysaccharides are quite stable against shear damage for typical conditions in conventional industrial emulsification, except when homogenization is done such that cavitation is present. Homogenization pressures required to affect such ingredients are much higher, and are then deliberately used to change the functionality of the macromolecules [138–141].

Besides the standard ingredients one can think of additives for functional foods, which can be dissolved molecules or particulates. The former quite probably have at least the shear stability of macromolecules. The latter might be encapsulated "goodies" or microbiological cells (living cultures). It is difficult to make general comments on the stability of encapsulates, given their variety and the dependence of their strength on product conditions like moisture level and pH. Typically, encapsulates will not be broken by pure simple shear, since their apparent viscosity ratio will be large and they will exhibit solid-body rotation rather than deformation and break-up. Added cultures usually are so-called gram-positive bacteria, which have a strong cell wall. Indeed the very high pressure homogenizers mentioned above are typically needed for the disruption of such cells [138].

7.5.3.2 **Effect on Product Structure**

It has been demonstrated in the literature that XME is a suitable method to produce double emulsions (oil-in-water-in oil, O/W/O, or water-in-oil-in-water, W/O/W) [142]. XME is then used to disperse the primary emulsion finely into the outer phase. The success of XME in this application is directly related to the mild processing conditions. In conventional emulsification, the requirement to have a rather small size of the droplets of the "outer" emulsion (W/O droplets in W/O/W) implies the use of high shear. Muguet *et al.* [143] have demonstrated that this implies an increased release of internal droplets. The Japanese company Morinaga has patented the use of XME for making duplex spreads in the early 1990s [110], although we are not aware that they actually have a product on the market.

In many cases, a structure is building up in the emulsion during emulsification. For instance, a fat–crystal network is starting to form in the oil phase of a margarine emulsion during cooling and emulsification in scraped-surface heat exchangers. In certain creams, a network of aggregated droplets is formed. When biopolymer mixtures are present, structure formation via phase separation and/or gelation can occur. These structure-formation processes are all affected by shear, and as can be expected the high shear required to set the droplet size is not always desired from the structure formation point of view. Using a mild emulsification method like XME might be beneficial in this context, although the structure formation in the continuous phase may well cause problems to mix the droplets uniformly into it.

7.5.4
Summary

It is frequently claimed or suggested in the ME literature that having a narrow DSD provides significant improvements in the properties of food products. The above considerations show that this is in fact far from obvious for many commercial food products. First, the properties of many products depend at least in part on the thickened and/or gelled continuous phase. Secondly, when focusing on the role of the DSD, we see that neither emulsion stability nor its rheology is significantly affected by the width of the DSD, except possibly the apparent emulsion viscosity in some cases. The claimed benefits of mild processing can be relevant for delicate ingredients and (micro)structures like encapsulated nutrients and flavors, but the standard ingredients like proteins and polysaccharides survive the shear in conventional processing quite well. An interesting area for ME is that of multiple-emulsion formation, as has also been pointed out by Charcosset [9]. Energy saving in emulsification has been demonstrated, but in foods its significance in the overall cost breakdown may often not be large enough to justify, on its own, a switch from conventional emulsification to ME. Moreover, it has to be noted that *total* energy expenditure needs to be considered, that is, it may be that large-scale ME lines require more frequent cleaning than conventional emulsification equipment.

7.6
Conclusions

ME and MCE are low energy input processes and have been successfully applied for the precision manufacture of particulate systems, however, efforts are required to develop further these worthwhile technologies for large-scale production. One of the biggest challenges is the development of novel surface properties of the membranes, needed to control their surface energy and avoid changes in wetting properties over time. Another important aspect concerns the reduction of membrane fouling during processing. It would be a big disadvantage if prefiltration of the droplet phase (in XME/MCE) or even of both phases (in PME) is needed, or if cleaning of the line needs to be done much more frequently than for conventional emulsification equipment. Increase in volume production could make these technologies competitive to conventional mechanical emulsification processes, allowing their process intensification and a sustainable production.

In several industries (e.g., pharmaceutical and fine chemicals) a narrow droplet-size distribution can be advantageous, as discussed in many review papers. However, in many food products the droplet-size distribution does not play a dominant role, and the size distributions that can be reached with conventional equipment are adequate. ME and MCE have potential for energy saving, but this can only be assessed fully if also changes in cleaning procedures are taken into account. If the latter does not add much, a quite significant energy saving for the emulsification process (close to an order of magnitude) seems achievable. Relative to the total energy expenditure in food manufacturing (which also includes energy-intensive steps like pasteurization) this may not be large, but in absolute terms it will contribute to a reduction of the carbon footprint.

Both ME and MCE processes have potential for the production of duplex emulsions. Up to now this has only been demonstrated at quite small scale, but a successful scale-up could lead to a range of novel food products.

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