Microemulsions: theoretical estimates of droplet sizes and size distributions

J. T. G. Overbeek

Van't Hoff Laboratory, University of Utrecht, The Netherlands

Abstract: After a brief introduction on general properties of microemulsions, this paper presents an expression for the Gibbs energy of a water in oil (W/O) microemulsion containing a range of droplet sizes. Droplets are partitioned in categories, j, where j is the number of surfactant molecules per droplet. The Gibbs energy takes into account: the amounts and chemical potentials of the constitutents of the dispersion medium and of the droplets, including the adsorption layers, the interfacial tension, the bending stress and the concentration of droplets of type j. The droplets of all sizes are in a mass-action equilibrium with single molecules in the water and/or oil regions. — A few necessary parameters are taken from experiments with the system: water, cyclohexane, sodium dodecylsulphate (SDS), 1-pentanol, and NaCl. — The concentration of droplets of type j can then be expressed in their radius, a_j, their surface tension and its dependence on curvature, and known constants (such as kT and parameters pertaining to the electrical double layer) both for saturated (Winsor II equilibria) and unsaturated microemulsions. — The size distributions are found to be fairly wide, the width increasing with increasing average droplet size.

Key words: Microemulsions; droplet sizes; size distribution; Winsor II equilibrium; curved interfaces; capillary pressure

Introduction

Microemulsions are mixtures of water, oil, relatively large amounts of one or more surfactants, and often electrolytes, all present in one thermodynamically stable phase. Their properties depend on their composition, but not on the method of preparation. They form spontaneously when the ingredients are brought together. In many cases microemulsions contain small droplets (diameter of the order of 20 nm) of one medium, e.g. water, W (or oil, O), dispersed in the other medium, O or W. There is a continuous transition from swollen micelles to microemulsion droplets. But, whereas in swollen micelles direct contact and interaction between surfactant and swelling agent exist, microemulsion droplets may be so large that most of their content is not in direct contact with the surfactant at the oil-water interface.

Systems in which microemulsions occur have complicated phase diagrams [1]. In this paper we shall concentrate on water in oil (W/O) droplet-type microemulsions, containing an ionic surfactant and a non-ionic "cosurfactant" (e.g., a medium chain length alcohol) [2—4] and on their phase equilibria with a non colloidal aqueous phase (Winsor II equilibrium) [5, 6].

In microemulsions the interfacial area between W and O is very large; therefore, the interfacial tension must be very low, so that the interfacial free energy can be compensated by the negative free energy of dispersion of the droplets in the medium. As a rule a sufficiently low interfacial tension is not obtained by the use of single chain ionic surfactants, since they form micelles before the interfacial tension is low enough. Addition of the cosurfactant, which lowers the interfacial tension in addition to the effect of the surfactant, allows the interfacial tension to drop to zero before micelles are formed [7].

By measuring the interfacial tension, σ, of a macroscopic oil-water interface as a function of the activities, a_i, of surfactant and cosurfactant their

surface excess concentrations, Γ_i, can be calculated from the Gibbs adsorption equation,

$$-\frac{\partial \sigma}{RT \, \partial \ln a_i} = \Gamma_i \, . \tag{1}$$

It is found that, at cosurfactant and electrolyte concentrations at which microemulsions can be formed, surfactant and cosurfactant show saturation adsorption, i.e., their surface concentrations are virtually independent of their bulk concentrations. Since, below the CMC the surfactant concentration is low and, assuming that the surface concentration at the curved surface of the droplets is not too different from that at a flat surface, the total area of the droplets can be found from the total amount of surfactant. Their total volume, V_d, is nearly equal to the total amount of water (for W/O microemulsions) and thus the radius a of the droplets, assumed to be of uniform size, is equal to

$$a = 3 \times \frac{\dfrac{4\pi a^3}{3}}{4\pi a^2} = \frac{3V_d}{A}$$

$$\cong \frac{3\bar{V}_w n_w \Gamma_{sa}(a)}{n_{sa}} \approx \frac{n_w}{n_{sa}} \, \text{\AA} \, . \tag{2}$$

In these equations A is the total area of the droplets, n_w and n_{sa} are the amounts of water and surfactant respectively, $\bar{V}_w$ is the molar volume of water and the last near equality implies that $\Gamma_{sa}(a) \cong 1.8 \, \mu$ mol m^{-2}, as has been found [7] for sodium-dodecylsulphate (SDS) at a flat ($a = \infty$) water-cyclohexane interface.

Equation (2) suggests that it should be possible to prepare thermodynamically stable emulsions with large droplets, e.g., with a radius of 1 μm, by choosing a large water-to-surfactant ratio. This, however, does not succeed. At given salt and cosurfactant activities, a given amount of surfactant can only solubilize a certain maximum amount of aqueous phase into a microemulsion. If more aqueous phase is offered it forms a separate phase in a so-called Winsor II equilibrium (W/O microemulsion + aqueous phase). This behavior can only be understood if the interface has a preferred curvature and a definite stiffness [6, 8—10]. At least two factors contribute to this stiffness, the crowding of the hydrocarbon chains of surfactant and cosurfactant in the interface, which tend to bend the inter-

face around the water, and the electric double layer at the water side, which tends to bend the interface around the oil.

These facts lead to the following model for microemulsions.

Model

We describe a W/O microemulsion as a suspension of spherical droplets, having a certain size distribution. The droplets contain all water and salt in the system and a small concentration ($\leqslant$ CMC) of the ionic surfactant. The interfacial adsorption layer contains all the ionic surfactant minus the small amount dissolved in the droplets, a sizable fraction of the cosurfactant, and the negative adsorptions of salt and oil. The Gibbs surface is chosen so that water is not adsorbed ($\Gamma_{water} = 0$). Since most of the ionic surfactant is in the interface, its concentration in the water can vary within fairly wide limits (zero to CMC) without much change in volume or interfacial area of the droplets. With any change in surfactant concentration the interfacial tension, σ, changes and thus we have the somewhat paradoxical situation that σ must be quite low to allow the existence of a microemulsion; however, σ is a parameter that adapts itself to variations in volume and area and, in particular, to changes in the concentrations of salt and cosurfactant [3].

Free energy of a microemulsion

In a previous paper [3] a thermodynamic analysis was given for a microemulsion with uniform droplet size. In this paper we follow the same line of thought, but introduce a particle-size distribution. The Gibbs free energy, G^M, of a droplet-type microemulsion can be written in two equivalent ways:

$$G^M = \sum_i n_i \mu_i = \sum_i n_{im} \mu_i + \sum_j n_{dj} \mu_{dj} \, . \tag{3}$$

n_i and μ_i are the total number of moles and the chemical potentials respectively of type i. n_{im} are the number of moles of type i in the continuous medium, n_{dj} and μ_{dj} are the number of droplets of category, j, and their chemical potential per droplet, respectively. The droplets are considered to also include the adsorption layers. j is defined as the

number of surfactant molecules in the adsorption layer of a single droplet with radius, a_j. This leads to the following relation between a_j and j:

$$j = 4\pi a_j^2 \Gamma_{sa,j} N_{Av} , \tag{4}$$

where N_{Av} is Avogadro's constant and $\Gamma_{sa,j}$ is the surface excess concentration at a droplet of radius a_j. It has been argued in [3] that the surface of constant (close) packing of surfactant and cosurfactant is a small distance, ξ (a few Å), away from the Gibbs surface for $\Gamma_w = 0$ and thus,

$$\Gamma_{sa,j} = \left(\frac{a_j + \xi}{a_j}\right)^2 \Gamma_{sa} , \tag{5}$$

where Γ_{sa} is the surface excess concentration at a flat surface.

Since the pressure inside and outside the droplets are, in general, different, we first formulate the Helmholtz free energy, F^M, of the microemulsion.

$$F_m = \sum_i n_{im}\lambda_{im} + \sum_i \sum_j n_{ij}\lambda_{ij} - pV_m$$
$$- \sum_j (p + \Delta p_j)V_{dj} + \sum_j \sigma_j A_j + F_{mix} , \tag{6}$$

where λ_{im} and λ_{ij} are the chemical potentials of i in the continuous medium and in the droplets of size j, respectively, when they are considered separately (i.e., not yet mixed, the medium at pressure, p, equal to the ambient pressure, the droplets at $p + \Delta p_j$). n_{im} and n_{ij} are the amounts of i in the continuous medium and in the droplets, j, respectively, n_{ij} containing both bulk and interface of the droplets. V_m is the volume of the medium, V_{dj} the volume of all droplets of type j. σ_j and A_j are the interfacial tension and the interfacial area of all droplets of type j. F_{mix} is the free energy of mixing of droplets and medium. It also contains a contribution of the preparation of the droplets from a macroscopic phase of suitable composition.

With the total volume of the microemulsion $V^M = V_m + \Sigma V_{dj}$ and assuming that $G_{mix} = F_{mix}$, we obtain

$$G^M = F^M + pV^M$$
$$= \sum_i n_{im}\lambda_{im} + \sum_{ij} n_{ij}\lambda_{ij} - \sum_j \Delta p_j V_{dj}$$
$$+ \sum_j \sigma_j A_j + G_{mix} . \tag{7}$$

In [3] an equation for G_{mix} was used that was valid up to quite high concentrations of uniform droplets. Modifying this equation for nonuniform droplet size is easy for low concentrations (ideal behavior), but gets complicated for higher concentrations because the interaction between the droplets depends on the concentrations of all droplets categories. Since essential effects of a droplet size distribution are already observed at low concentrations, we shall limit the treatment here to ideal behavior, and we write for G_{mix}

$$G_{mix} = \sum_j n_{dj}kT$$
$$\times \left(\ln \frac{n_{dj} \times \frac{4}{3}\pi a_j^3}{V^M} - 1 \right.$$
$$\left. + \frac{3}{2} \ln \frac{v_w}{16 a_j^3} \right) , \tag{8}$$

where k is the Boltzmann constant, v_w is the volume of a water molecule, and the term $1.5 \ln(v_w/16a_j^3)$ reflects Reiss's [11, 12] treatment of the formation of the droplets from a bulk solution of the same composition.

Introducing

$$\Delta p_j = \frac{2\sigma_j}{a_j} - \frac{2c_j}{a_j^2} , \tag{9}$$

$$A_j = n_{dj} \times 4\pi a_j^2 , \tag{10}$$

and

$$V_{dj} = n_{dj} \times \frac{4}{3}\pi a_j^3 , \tag{11}$$

where the bending stress coefficient, c_j, of the interfaces is defined as

$$c_j \equiv (\partial\sigma/\partial(2/a))_{a=a_j} , \tag{12}$$

we can write Eq. (7) as

$$G^M = \sum_i n_{im}\lambda_{im} + \sum_{ij} n_{ij}\lambda_{ij} + \sum_j \frac{4}{3}\pi a_j^2 n_{dj}$$
$$\times \left(\sigma_j + \frac{2c_j}{a_j} \right) + G_{mix} . \tag{13}$$

Now we want to find out at what size distribution the system is in equilibrium, i.e., under what conditions G^M has a minimum value. By combining Eqs. (3), (8), and (13) we can find an expression (Eq. (17)) for the chemical potential, μ_{dj}, of the droplets of size j, which contains the concentration n_{dj}/V^M. We can also find μ_{dj} with a mass-action approach, as the sum of the chemical potentials of all the constituents of the droplets (Eq. (18)). Elimination of μ_{dj} between the two equations (17) and (18) then solves our problem, at least in principle. Combination of Eqs. (3), (8), and (13) leads to

$$
\begin{aligned}
G^M = {} & \sum_i n_{im}\mu_i + \sum_j n_{dj}\mu_{dj} \\[4pt]
= {} & \sum_i n_{im}\lambda_{im} + \sum_{i,j} n_{ij}\lambda_{ij} + \sum_j \frac{4}{3}\,\pi a_j^2 \\[4pt]
& \times \left(\sigma_j + \frac{2c_j}{a_j} \right) n_{dj} + \sum_j n_{dj}kT \\[4pt]
& \times \left(\ln \frac{n_{dj} \times \dfrac{4}{3}\,\pi a_j^3}{V^M} - 1 \right. \\[4pt]
& \left. + \frac{3}{2}\ln \frac{v_w}{16 a_j^3} \right).
\end{aligned}
$$

(14)

The difference between μ_i and λ_{im} of the continuous medium is found by differentiation of G^M with respect to n_{im} at constant $n_{km}(k \neq i)$ and n_{dj}:

$$
\begin{aligned}
\left(\frac{\partial G^M}{\partial n_{im}} \right) &= \mu_i \\[6pt]
&= \lambda_{im} - \frac{\sum\limits_j n_{dj}kT}{V^M}\,\frac{\partial V^M}{\partial n_{im}} \\[6pt]
&= \lambda_{im} - \frac{\sum\limits_j n_{dj}kT}{V^M}\,\bar{V}_i ,
\end{aligned}
$$

(15)

where $\bar{V}_i$ is the molar volume of i. And thus,

$$
\begin{aligned}
\sum_i n_{im}\mu_i ={} & \sum_i n_{im}\lambda_{im} \\[4pt]
& - \left(\sum n_{dj}kT \right) \times (1 - \varphi),
\end{aligned}
$$

(16)

where φ is the volume fraction of the droplets. From Eqs. (14) and (16) it follows then that

$$
\begin{aligned}
\mu_{dj} ={} & \sum_i \frac{n_{ij}\lambda_{ij}}{n_{dj}} + \frac{4}{3}\,\pi a_j^2 \left(\sigma_j + \frac{2c_j}{a_j} \right) + kT \\[6pt]
& \times \left(\ln \frac{n_{dj} \times \dfrac{4}{3}\,\pi a_j^3}{V^M} - \varphi \right. \\[6pt]
& \left. + \frac{3}{2}\ln \frac{v_w}{16 a_j^3} \right),
\end{aligned}
$$

(17)

and from mass action,

$$
\mu_{dj} = \sum_i \frac{n_{ij}}{n_{dj}}\,\mu_i .
$$

(18)

φ might be dropped from Eqs. (16) and (17) with the argument that other terms also proportional to φ would appear in these equations as soon as droplet interaction is not neglected. The conditions (16) through (18) also guarantee that G^M is at a minimum for constant p, T, and all n_i.

It is awkward that in Eq. (17) each particle category, j, has its own values for λ_{ij}, σ_j, and c_j: However, in a system with a given composition of the water and the oil regions σ and c are fairly simple functions of the radius of curvature, a. As has been argued in [3], σ has a more or less parabolic shape with a minimum when plotted against $1/a$ and c is an increasing function of $1/a$ when a is called positive for interfaces curving around the aqueous medium. In [3] a linear relation between c and $1/a$ gave satisfactory results. Fig. 1 gives a sketch of the situation.

We thus write:

$$
c = -b + \frac{d}{a}
$$

(19)

and, using Eq. (12)

$$
\sigma = \sigma_\infty - \frac{2b}{a} + \frac{d}{a^2} .
$$

(20)

In these relations d was shown to be practically independent of salt- and cosurfactant concentrations in W/O microemulsions consisting of water, cyclo-
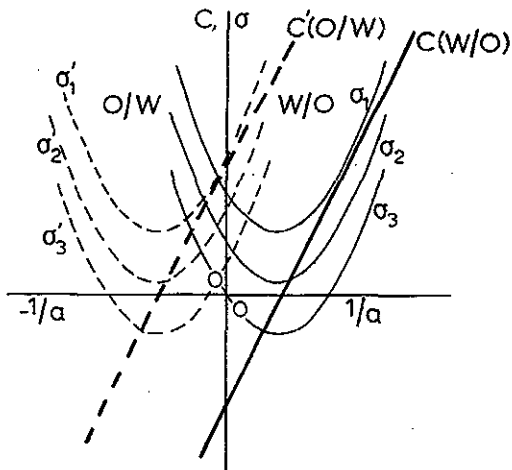
Fig. 1. Interfacial tension, σ, and bending stress coefficient, c, plotted against the curvature (= reciprocal radius, $1/a$). The drawn lines refer to a W/O situation where the preferred curvature is around the water. The broken lines refer to O/W. The three values for the interfacial tension all lead to the same line for c, showing that for fixed c, σ can still vary greatly

hexane, NaCl, sodium dodecylsulphate (SDS), and 1-pentanol. b is positive for W/O, increases with NaCl and cosurfactant concentrations, and it is zero for conditions where W/O goes over into O/W. σ_∞ is adapted to equilibrium conditions by changes in the small SDS concentration. The droplets consist of bulk, of volume $4/3\pi a_j^3$ and an adsorption layer of area $4\pi a_j^2$. The bulk contains all water, the ionic surfactant minus its adsorption, and the NaCl plus *the negative adsorption of the coions* (we neglected the solubilities of oil and cosurfactant in the aqueous medium). In the surface layer all adsorbed surfactant and cosurfactant are present, with the negative adsorption of the salt and, to obtain zero volume, the negative adsorption of the oil. Writing

$$x = \Gamma_{sa}\bar{V}_{\text{SDS}} + \Gamma_{\text{Cl}}\bar{V}_{\text{NaCl}} , \qquad (21)$$

(where sa stands for the surfactant ion) for the equivalent thickness of the adsorption layers of surfactant and salt, we find the components, water, surfactant, and salt in the volume

$$\sum_{\substack{\text{water} \\ \text{SDS} \\ \text{NaCl}}} \frac{n_{ij}}{n_{dj}} \bar{V}_i = \frac{4}{3}\pi a_j^3 + 4\pi a_j^2 x . \qquad (22)$$

For these components, λ_{ij}, being the chemical potential at the pressure $p + \Delta p_j$ in a stagnant droplet, can be written

$$\lambda_{ij} = \mu_i' + \Delta p_j \bar{V}_i = \mu_i' + \left(\frac{2\sigma_j}{a_j} - \frac{2c_j}{a_j^2}\right)\bar{V}_i , \qquad (23)$$

where $\bar{V}_i$ is the partial molar volume of component i and μ_i' is its chemical potential at the ambient pressure p. Since the bulk composition of the droplets may be assumed not to depend on their size, μ_i' does not depend on j. It differs from the chemical potential μ_i in the microemulsion as a whole, since μ_i' does not contain a contribution from G_{mix} and μ_i does. The adsorbed cosurfactant and the negatively adsorbed oil belong to the droplet, but their chemical potential is the same as in the continuous medium at pressure p.

By elimination of μ_{dj} from Eqs. (17) and (18) and use of Eqs. (19)—(23), Eq. (24) is obtained.

$$\ln\frac{n_{dj}}{V^M} = \ln\frac{48 a_j^{3/2}}{\pi v_w^{3/2}} - \frac{4\pi d - 8\pi x b}{kT}$$

$$+ \frac{8\pi a_j}{kT}(b - x\sigma_\infty) - \frac{4\pi a_j^2}{kT}\sigma_\infty$$

$$+ \left(\sum_i \frac{n_{ij}}{n_{dj}} \frac{\mu_i - \mu_i'}{kT}\right)_{i\,=\,\text{water, SDS, NaCl}} . \qquad (24)$$

The term with $\mu_i - \mu_i'$ does not contain contributions from oil and cosurfactant, since for these components μ_i and μ_i' differ by a factor proportional to the droplet concentration that should be neglected for small volume fractions (say < 0.05).

In [3] it was shown that $(\mu_i - \mu_i')/\bar{V}_i$ does not depend on i. Therefore, we may write

$$\sum_i \frac{n_{ij}\bar{V}_i}{n_{dj}} \frac{\mu_i - \mu_i'}{\bar{V}_i kT} = -\left(\frac{4\pi}{3}a_j^3 + 4\pi a_j^2 x\right) MU , \qquad (25)$$

where $MU = (\mu_i' - \mu_i)/(\bar{V}_i kT)$, ($i$ = water, SDS, NaCl).

MU, being proportional to $\mu_i' - \mu_i$ for the aqueous components, is zero for saturated microemulsions, for at the Winsor II equilibrium the composition of the bulk of the droplets and the equilibrium aqueous phase are identical, and the chemical potentials μ_i' and μ_i are both at ambient pressure.

For unsaturated microemulsions, MU is positive, because such microemulsions will spontaneously take up a solution, that has the composition of the bulk of the droplets and, thus, $\mu'_i > \mu_i$.

Values for Γ_{sa}, d, and x are known from our previous work [3]. For the system water, cyclohexane, SDS, pentanol, and NaCl, Γ_{sa} varies from 2.0×10^{-6} mol m^2 for 4.11% pentanol in cyclohexane and 0.3 M NaCl, to 1.56×10^{-6} mol m^{-2} for 19% pentanol and 0.1 M NaCl, d, the slope of the c vs $1/a$ line (Eq. (19)) is about 2.5 to 3.0 kT and x (Eq. (21)) = 0.4 nm.

On the assumption that the influence of the hydrocarbon tails on c is constant at constant cosurfactant activity, $-b$, the cut-off of c for $1/a = 0$ is obtained from the influence of NaCl on the Winsor II equilibrium and varies from $-0.51 \cdot 10^{-12}$ N for 19% pentanol and 0.3 M NaCl to zero for 19% pentanol, and 0.15 M NaCl or for 7.65% pentanol and 0.3 M NaCl.

These values have been found from an analysis in which all drops were assumed to have the same size, but they should also be good approximations if a size distribution is present.

Furthermore, as mentioned before, σ_∞ (Eq. (20)) must adapt itself by changes in the small SDS concentration to the volume (in essence the amount of water) and the interfacial area (given by the amount of SDS) of the droplets.

Finally, MU, reflecting the difference between μ'_i and μ_i that is due to the free energy of mixing, changes even at constant composition of the oil and water media by changes in the volume fraction and interfacial area and, thus, in the sizes and numbers of the droplets.

Results in terms of calculated size distributions

On the basis of Eqs. (24) and (25) a simple computer programm can be set up for calculating the size distribution, n_{dj}/V^M vs. a_j or, easier vs $j = 4\pi(a_j + \xi)^2 \Gamma_{sa} N_{Av}$ since each integer j corresponds to one size category of droplets.

Γ_{sa} and x are known from experiments. When ξ is chosen (within narrow limits, see [3]), b follows from experiments. Then MU is set equal to zero, so as to obtain a microemulsion in Winsor II equilibrium, and preliminary values of d and σ_∞ are chosen, d being slightly larger than the value found for uniform droplets (the concentrations of the categories j are much smaller than the concen-

tration of particles if all are uniform) and σ_∞ based on the condition for internal equilibrium in an emulsion with uniform droplets (Eq. (33) in [3]).

After calculating n_{dj}/V^M from Eq. (24) for all relevant values of a_j or j (n_{dj} is small for small and for large values of j with a single maximum in between) the total area ($\Sigma\ 4\pi a_j^2 n_{dj}$), the total amount of surfactant ($\Sigma\ 4\pi(a_j + \xi)^2 \Gamma_{sa} n_{dj}$) and the total droplet volume ($\Sigma\ 4\pi a_j^3 n_{dj}/3$) can be found. An important average radius, $\langle a \rangle$, comparable to "the" droplet radius of Eq. (2) is

$$
\langle a \rangle = \frac{\sum 4\pi a_j^3 n_{dj}}{\sum 4\pi (a_j + \xi)^2 n_{dj}}
$$

$$
= \frac{3 \sum_j V_{dj} \Gamma_{sa}}{n_{sa}} \cong \frac{n_w}{n_{sa}}\ \text{Å} .
\tag{26}
$$

The values obtained can be compared with experimental data. If necessary, a better fit can be reached by adapting σ_∞ and, to a lesser extent, d, until the droplet volume and the total amount of surfactant agree with experiments.

In a next step the calculation is repeated for an unsaturated microemulsion, keeping the composition of water and oil regions constant, and thus keeping Γ_{sa}, b, d, x and ξ constant, but choosing finite positive values for MU and adapting σ_∞, so that, for example the total droplet volume is halved, the total amount of surfactant in the interface is kept constant, and thus the average droplet radius is about halved too. Good tentative values for MU and σ_∞ can again be obtained from the results in [3] for uniform droplets (esp. Eqs. (33) and (46)).

In Figs. 2 and 3 and in Table 1, we show a few typical results obtained in this way. The *size distributions are fairly wide*. They become narrower (relatively narrower) for smaller average droplet size, irrespective of whether the smaller droplets are obtained by making the microemulsions unsaturated at constant composition of the water and oil regions, or by increasing salt and/or cosurfactant concentration, but keeping at the Winsor II boundary, where MU is zero.

Another obvious application consists in checking how droplet size is affected by changing the surfactant concentration (or, equivalently, the volume fraction, φ) in Winsor II equilibria. It is found that the average droplet size decreases with decreasing concentration as might be expected on qualitative
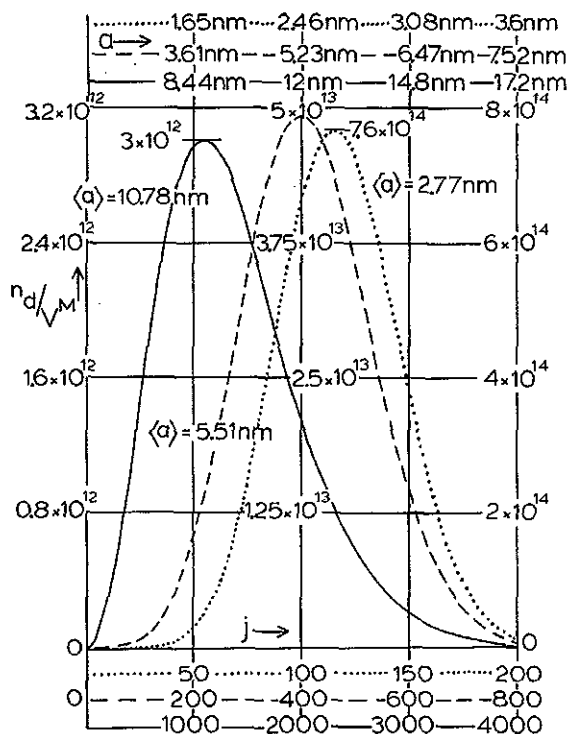
Fig. 2. Number of droplets of category j per cm^3 (n_{dj}/V^M) according to Eq. (24) plotted against j (linear scale) or a_j (non linear scale). The units on the horizontal and vertical axis have been chosen so as to give the curves about the same maximum height and about the same width. The data correspond to microemulsions of 0.2 M NaCl in water in 19% (w/w) 1-pentanol in cyclohexane. Detailed data are collected in Table 1

Fig. 3. As for Fig. 2, except that the data correspond to 0.3 M NaCl

arguments. At high dilution the entropy of mixing becomes relatively more important and favors a larger number of smaller droplets. The effect is quite marked, especially at low concentrations, but not as pronounced as with uniform droplets.

Table 2 compares the average radius $\langle a \rangle$ (Eq. (26)) for a series of volume fractions φ, with radii a of uniform droplets at corresponding values of V_{hs}/V^M, where V_{hs} is the total volume of hard spheres. V_{hs}/V^M is larger than φ in the ratio (1 + 24 Å/$\langle a \rangle$) (See [3], Eqs. (31) and (35)), because V_{hs} also contains the adsorbed layers of surfactant and cosurfactant. No attempt has been made to match $\langle a \rangle$ and a for a particular volume fraction. This could have been easily achieved by simultaneous small changes in d and σ_∞.
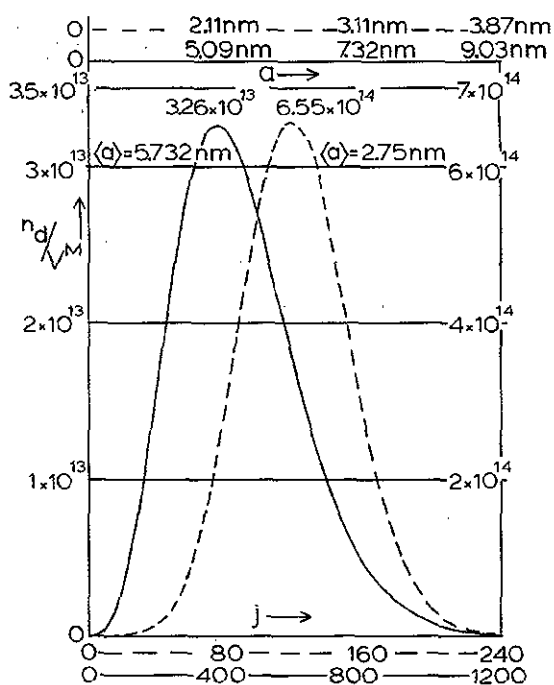
Discussion

It may be useful to discuss qualitatively the size distribution following from Eqs. (24) and (25). If the free energy of mixing is neglected the droplet size would tend to be uniform at $c = 0$, i.e., at $a = d/b$ and σ would adapt to zero, too. The free energy of mixing causes the droplets to be smaller than $a = d/b$, because that implies a gain in entropy. Very small droplets are unfavorable, since for them the surface free energy (in particular the $(d/a^2) \times 4\pi a^2 \times n_d$ term) becomes too high. Somewhat larger droplets are present in larger numbers, in the first instance due to the $a_j^{3/2}$ term, which reflects the fact that the center of mass of a larger droplet gains more freedom in being dispersed in the volume V^M than a smaller droplet. This idea is due to Reiss [11, 12] and also explained in [3]. At further increase of the droplet size the advantage given by the $a_j^{3/2}$ term is offset and more than offset by the increase in the surface free energy, in particular by the $4\pi a_j^2 \times \sigma_\infty$ term and still more strongly by the MU term, which is proportional to the droplet volume and which reflects the fact that more material has to

Table 1. Data used for the calculation of the size distributions in Figs. 2 and 3 with Eq. (24) and results from these calculations

For all curves: ζ (Eq. (5)) = 0.3 nm; x (Eq. (21)) = 0.4 nm; d (Eq. (19)) = 2.8 kT; $\Sigma\, jn_{dj}/V^M$ = 1.03443 × 10^{-5} mol SDS/cm^3 = 2.982 g SDS/l.

For curves at 0.2 M NaCl: Γ_{sa} (Eqs. (1) and (5)) = 1.73 μ mol m^{-2}; b (Eq. (19)) = 1.8 × 10^{-13} N.

		MU/nm^{-3} Eq. (25)	σ_∞/mN m^{-1} Eq. (20)	A/m^2 cm^{-3} Eq. (2)	φ Eq. (16)	$\langle a \rangle$/nm Eq. (26)
No. 1	Saturated	0	0.0225	5.643	0.02028	10.782
No. 2	1/2 Saturated	0.01516	−0.13367	5.3647	0.009856	5.512
No. 3	1/4 Saturated	0.18	−1.02758	4.8500	0.004472	2.766

	Max. $(n_{dj} \times$ cm$^3)/V^M$	at a_j/nm	Width = $(a(0.9\,\varphi) - a(0.1\,\varphi))/a(0.5\,\varphi)$
No. 1	3.003 × 10^{12}	8.837	0.532
No. 2	4.934 × 10^{13}	5.207	0.356
No. 3	7.640 × 10^{14}	2.64	0.308

For curves at 0.3 M NaCl: Γ_{sa} = 1.82 μ mol m^{-2}; b = 5.1 × 10^{-13} N

		MU/nm^{-3}	σ_∞/mN m^{-1}	A/m^2 cm^{-3}	φ	$\langle a \rangle$/nm
No. 4	Saturated	0	0.104763	5.109	0.009764	5.732
No. 5	1/2 Saturated	0.132	−0.607087	4.602	0.004218	2.750

	Max. $(n_{dj} \times$ cm$^3)/V^M$	at a_j/nm	Width = $(a(0.9\,\varphi) - a(0.1\,\varphi))/a(0.5\,\varphi)$
No. 4	3.261 × 10^{13}	4.946	0.482
No. 5	6.555 × 10^{14}	2.627	0.334

Table 2. Influence of the droplet concentration on the (average) radius of the droplets

Volume fraction φ	Average radius, Eq. (26) $\langle a \rangle$/nm	Hard sphere Volume fraction V_{hs}/V^M corresp. to φ	Radius of mono-dispersed droplets, a/nm, [3]
0.080383	6.552	0.10983	6.463
0.037114	6.246	0.051374	6.015
0.018249	5.970	0.025584	5.656
0.0097641	5.733	0.013852	5.361
0.0017292	5.096	0.0025436	4.593
0.00066199	4.756	0.00099603	4.186

be brought from μ_i to μ_i' ($\mu_i < \mu_i'$) in the building of larger droplets. Or, in other words, the standard chemical potential of larger droplets is higher than that of smaller droplets as a consequence of surface effects and volume effects, but the reverse is the case, due to the Reiss effect connected with the formation of individual droplets from a bulk phase.

Very little *experimental information* on the droplet size distribution in the system studied here (water, cyclohexane, SDS, 1-pentanol, NaCl) is available, but preliminary SAXS measurements show that the W/O microemulsions are not monodispersed, but have a size distribution with a width of at least 20% in the radius [13].

A change in the average size with the droplet concentration has not been found experimentally, but the size range tested was higher than corresponds to Table 2, and at the higher concentrations in that table hard sphere interactions are probably already not negligible.

Finally, I want to point out that after I had presented a preliminary version of this paper in April 1989, Prof. H.-F. Eicke showed me the typescript of his paper (meanwhile published [14]) treating droplet-size distribution in microemulsions. In general the two approaches are similar, but many important details are different. In [14] a fairly wide size distribution is also found.

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Author's address:

Prof. J. Th. G. Overbeek
Van't Hoff Laboratory
University of Utrecht
Padualaan 8
3584 CH Utrecht, The Netherlands