Available online at www.sciencedirect.com

ScienceDirect

Colloids and Surfaces A: Physicochem. Eng. Aspects 295 (2007) 91–98

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

# Estimation of the distribution of droplet size, interfacial area and volume in emulsions

Encarnación Jurado*, Vicente Bravo, Fernando Camacho, José M. Vicaria, Alejandro Fernández-Arteaga

*Departamento Ingeniería Química, Facultad Ciencias, Campus Universitario Fuentenueva, Universidad de Granada, Avda. Fuentenueva, s/n, 18.071 Granada, Spain*

Received 5 May 2006; received in revised form 27 July 2006; accepted 14 August 2006

Available online 22 August 2006

## Abstract

A two-parameter equation to reproduce the droplet size distribution (DSD) of emulsions has been developed. The equation has been applied satisfactorily to oil-in-water (O/W) emulsions with triolein and tributyrin as oil phase and gum arabic, an alkylpolyglucoside and a fatty ethoxilated alcohol as emulsifier agents. Emulsions with aging effect also have been studied. The equation reproduces satisfactorily the DSD obtained using two parameters, *n* and *m*. This equation enables to determine the distribution of the interfacial area and the oil volume in the emulsions prepared. The equation is suitable too to model the experimental results reported by different researchers.

© 2006 Published by Elsevier B.V.

*Keywords:* Droplet size distribution; Emulsions; Interfacial area

## 1. Introduction

Emulsions are fundamental in many applications (food processing, petroleum and detergents industries) [1] and industrial products (foods, pharmaceuticals or cosmetics) [2]. In specific, oil-in-water (O/W) emulsions are used in industrial operations involving two immiscible fluids and emulsifier agents which allow emulsion formation and stabilization [3].

The droplet size distribution influences the properties of the emulsion in aspects such as degradation rates, long-term stability, resistance to creaming [4,5], texture and optical appearance [6], viscosity, physiological efficiency [4,5], and chemical reactivity as, for example, in the kinetics of polymerization reactions [7] or in lipase catalysed reactions where the interfacial area between oil/aqueous phase has a strong influence [8].

One common way to characterize the size distribution of the emulsions is the use of parameters that indicate the dispersion, such as median drop size [9], Sauter diameter [10], and diameter of the largest stable drop size [11]. Although these are commonly used, they are not very suitable for characterizing emulsions because they fail to provide all the information of the system and thus provide only an approach. For an accurate determination of the most characteristic parameters of the emulsions (total distribution of droplet surface, volume or mass), it becomes necessary to evaluate the droplet size distribution (DSD) of an emulsion. If the parameters of the distribution function can be related to the emulsification process or the properties of the resulting emulsion, still more useful information can result.

A wide variety of mathematical and empirical distribution functions, such as the normal distribution, log-normal distribution, Rosin-Rammler equation, Nukiyama-Tanasawa equation, etc. have commonly been used to simulate the DSD [12] in different processes, such as atomization or spraying. In emulsions, where mechanical stirring is very commonly employed to generate fine drops in another liquid and to maintain the dispersion of the drops generated [1], different models have been commonly used also to simulate the DSD. The normal distribution does not usually show a good fit to the experimental results, since the distributions are rarely symmetrical. One of the most common methods used is the lognormal distribution [7,13], which in some cases provides a satisfactory correlation [7].

---

* Corresponding author. Tel.: +34 958 243307; fax: +34 958 248992.
*E-mail address:* ejurado@ugr.es (E. Jurado).

0927-7757/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.colsurfa.2006.08.037

Another model used to reproduce a DSD is the Rosin-Rammler equation [14]:

$$1 - V_{\mathrm{cum}} = \exp\left(-\left(\frac{d_i}{a}\right)^b\right) \tag{1}$$

where $a$ and $b$ are the parameters of the distribution and $V_{\mathrm{cum}}$ is the cumulative volume fraction of the drops that have diameters less than $d_i$. This equation is useful for engineering calculations [15]. Karabelas [16] found that $b$ varied between 2.3 and 2.9. To determine microsphere-sized distribution function Bahukudumbi et al. [17] also used the Rosin-Rammler distribution, considering the distribution function of the number of droplets normalized $F_{\mathrm{nI}}$, instead $V_{\mathrm{cum}}$ (Eq. (2)), finding that $a$ and $b$ had values of between 1.2 and 5.0.

$$F_{\mathrm{nI}}(d_i) = 1 - \exp\left(-\left(\frac{d_i}{a}\right)^b\right) \tag{2}$$

Another widely used equation to determine the particle-size distribution in different processes (atomization, dryers, etc.) is the Nukiyama and Tanasawa equation [18]:

$$f_{\mathrm{nI}}(\delta) = K\delta^n \exp(-k\delta^m) \tag{3}$$

where $\delta$ is the dimensionless diameter, $f_{\mathrm{nI}}$ is the droplet size distribution function and $K$, $n$, $k$ and $m$ are empirical parameters. The equation may be expected to have at least some application in emulsions, although it is difficult to use because it is necessary to determine four empirical parameters.

In the present study, a modification of the Nukiyama and Tanasawa equation is proposed to reproduce the DSD of the emulsions by using the Sauter diameter and only two empirical parameters ($n$ and $m$). The equation proposed reproduces the experimental results of O/W emulsions prepared with triolein and tributyrin by mechanical stirring using gum arabic, an alkylpolyglucoside and a fatty ethoxilated alcohol as emulsifier agents, while being applied also to determine the distribution of the interfacial area as well as the distribution of the volume in the emulsion. In addition, the results reported by other researchers are reproduced. This equation fits the experimental data more satisfactorily than do other DSD models.

## 2. Materials and methods

Triolein and tributyrin were used as oil phases. Triolein is glycerol trioleate ($C_{57}H_{104}O_6$; MW = 885.5 g/mol, $\rho = 0.91$ g/cm$^3$), a natural liquid oil practically insoluble in water and widely used as a soily model in detergency. It was supplied by Sigma (practical grade) and the concentration assayed was between 1 and 5 wt.%. Tributyrin is a glycerol tributyrate ($C_{15}H_{26}O_6$; MW = 302.4 g/mol, $\rho = 1.03$ g/cm$^3$) a liquid oil used in kinetic studies with lipases. It was supplied by Panreac (purity > 99%) and the concentration assayed was between 1and 5 wt.%.

The emulsifier agent was a solution of NaCl (18.1 g/L), $KH_2PO_4$ (0.41 g/L), glycerine (54%, v/v), deionized water (Milli-Q®, Millipore) and gum arabic (a natural polysaccharide used commonly as stabilizer in different food, cosmetics and pharmaceutical O/W emulsions due to the increasing of the viscosity of the system [19]) supplied by Merck. The concentration of gum arabic studied was between 1 and 5 g/L. Emulsions were prepared with other emulsifier agents. In one of them, the oil phase was emulsified with 0.2 g/L of Glucopon 650 (an alkylpolyglucoside) supplied by Henkel-Cognis; in the other emulsion the oil phase was emulsified with 0.2 g/L of Findet1214N23 (a fatty ethoxilated alcohol) supplied by Kao Corporation.

The emulsions were prepared by adding the emulsifier agent in the disperse phase. The components were prepared by mechanical stirring (1 min, 13,000 rpm) with an Ultraturrax-T25 (Ika-Werke). The DSD measurement was made at 25 °C by laser diffraction with a Coulter LS-230 analyser (Beckman Coulter Company). The collected scattered intensity as a function of the angle is converted into the size distribution using the Mie theory.

## 3. Theory

The normalized diameter ($\delta$) used in Eq. (3) is calculated as:

$$\delta = \frac{d_i}{D_{32}} \tag{4}$$

where $d_i$ is the droplet diameter. The Sauter diameter ($D_{32}$) is defined as:

$$D_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \tag{5}$$

and $n_i$ is the number of droplets between two consecutive diameters.

Eq. (3) needs the values of $n$, $m$ and $k$, since $K$ is a normalizing parameter. The $K$ value is determined from the number of droplets per volume unit, $n_{\mathrm{B}}$:

$$n_{\mathrm{B}} = \sum_i n_i = \int_0^\infty f_{\mathrm{nI}}(\delta)\,\mathrm{d}\delta \tag{6}$$

Replacing Eq. (3) in Eq. (6):

$$n_{\mathrm{B}} = K\int_0^\infty \delta^n \exp(-k\delta^m)\,\mathrm{d}\delta \tag{7}$$

replacing in this equation the variable $y = k\delta^m$, where:

$$\mathrm{d}y = mk\delta^{m-1}\,\mathrm{d}\delta \qquad \delta = \left(\frac{y}{k}\right)^{1/m} \tag{8}$$

and considering the gamma function definition ($\Gamma$):

$$\Gamma\left(\frac{n+1}{m}\right) = \int_0^\infty y^{((n+1)/m)-1} \exp(-y)\,\mathrm{d}y \tag{9}$$

the integration of the Eq. (7) is transformed into:

$$\int_0^\infty \delta^n \exp(-k\delta^m)\,\mathrm{d}\delta = \frac{1}{mk^{(n+1)/m}}\Gamma\left(\frac{n+1}{m}\right) \tag{10}$$

and finally:

$$K = n_{\mathrm{B}}\frac{mk^{(n+1)/m}}{\Gamma((n+1)/m)} \tag{11}$$

Replacing Eq. (11) in Eq. (3), the DSD function would be:

$$f_{\mathrm{nI}}(\delta) = n_{\mathrm{B}}\frac{mk^{(n+1)/m}}{\Gamma((n+1)/m)}\delta^{n}\exp(-k\delta^{m}) \tag{12}$$

However, $n$, $m$ and $k$ are not independent. Replacing Eqs. (4) and (6) in Eq. (5):

$$D_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} = \frac{\int_0^\infty D_{32}^3\delta^3 f_{\mathrm{nI}}(\delta)\,\mathrm{d}\delta}{\int_0^\infty D_{32}^2\delta^2 f_{\mathrm{nI}}(\delta)\,\mathrm{d}\delta} \Rightarrow 1 = \frac{\int_0^\infty \delta^3 f_{\mathrm{nI}}(\delta)\,\mathrm{d}\delta}{\int_0^\infty \delta^2 f_{\mathrm{nI}}(\delta)\,\mathrm{d}\delta} \tag{13}$$

considering Eq. (3) and (11), and operating in a similar form to Eq. (10), it is obtained $k$ from Eq. (13):

$$k = \left(\frac{\Gamma((n+4)/m)}{\Gamma((n+3)/m)}\right)^{m} \tag{14}$$

this enables to calculate $k$ with $n$ and $m$.

The DSD function, Eq. (12), can be expressed as the fraction of droplets dividing by $n_{\mathrm{B}}$, defining the distribution function of the number of droplets normalized ($F_{\mathrm{nI}}$) of $\delta$-sized droplets as:

$$F_{\mathrm{nI}}(\delta) = \frac{f_{\mathrm{nI}}(\delta)}{n_{\mathrm{B}}} = \frac{mk^{(n+1)/m}}{\Gamma((n+1)/m)}\delta^{n}\exp(-k\delta^{m}) \tag{15}$$

Therefore, substituting Eq. (14) in Eq. (15), the n and m values for a DSD could be estimated.

If this expression is derived and made equal to zero, it is possible to determine $\delta$ in which the DSD reach a maximum, which could be calculated by:

$$\delta_{\max} = \left(\frac{n}{mk}\right)^{1/m} \tag{16}$$

The distribution function of the oil-phase volume normalized ($F_{\mathrm{vI}}$) of $\delta$-sized droplets could be determined by considering Eq. (12) in the fraction of volume of emulsion occupied by the oil phase ($\varepsilon_{\mathrm{oil}}$) defined as:

$$\begin{aligned}\varepsilon_{\mathrm{oil}} &= \int_0^\infty \frac{\pi}{6}D_{32}^3\delta^3 f_{\mathrm{nI}}(\delta)\,\mathrm{d}\delta \\ &= \frac{\pi}{6}D_{32}^3 n_{\mathrm{B}}\frac{mk^{(n+1)/m}}{\Gamma((n+1)/m)}\int_0^\infty \delta^{n+3}\exp(-k\delta^{m})\,\mathrm{d}\delta\end{aligned} \tag{17}$$

and in a similar way as in Eq. (10):

$$\varepsilon_{\mathrm{oil}} = n_{\mathrm{B}}\frac{\pi}{6}D_{32}^3\frac{\Gamma((n+4)/m)}{\Gamma((n+1)/m)}k^{-3/m} \tag{18}$$

where upon $F_{\mathrm{vI}}$ could be calculated as:

$$F_{\mathrm{vI}}(\delta) = \frac{(\pi/6)D_{32}^3\delta^3 f_n(\delta)}{\varepsilon_{\mathrm{oil}}} = \frac{mk^{(n+4)/m}}{\Gamma((n+4)/m)}\delta^{n+3}\exp(-k\delta^{m}) \tag{19}$$

The distribution function of the interfacial area normalized ($F_{\mathrm{aI}}$) of $\delta$-sized droplets could be determined considering Eq. (12) in the interfacial area per volume unit of the emulsion ($a_{\mathrm{oil}}$) defined as:

$$\begin{aligned}a_{\mathrm{oil}} &= \int_0^\infty \pi D_{32}^2\delta^2 f_{nI}(\delta)\,\mathrm{d}\delta \\ &= \pi D_{32}^2 n_{\mathrm{B}}\frac{mk^{(n+1)/m}}{\Gamma((n+1)/m)}\int_0^\infty \delta^{n+2}\exp(-k\delta^{m})\,\mathrm{d}\delta\end{aligned} \tag{20}$$

and in a similar way as in Eq. (10):

$$a_{\mathrm{oil}} = n_{\mathrm{B}}\pi D_{32}^2\frac{\Gamma((n+3)/m)}{\Gamma((n+1)/m)}k^{-2/m} \tag{21}$$

whereupon $F_{\mathrm{aI}}$ could be calculated as:

$$F_{\mathrm{aI}}(\delta) = \frac{\pi D_{32}^2\delta^2 f_{\mathrm{nI}}(\delta)}{a_{\mathrm{oil}}} = \frac{mk^{(n+3)/m}}{\Gamma((n+3)/m)}\delta^{n+2}\exp(-k\delta^{m}) \tag{22}$$

The $n$ and $m$ parameters are calculated applying Eqs. (14) and (15) to the experimental data. It could allow for determining $F_{\mathrm{vI}}$ and $F_{\mathrm{aI}}$ in Eqs. (19) and (22) respectively. Knowing $\varepsilon_{\mathrm{oil}}$, it is evaluated $n_{\mathrm{B}}$ with Eq. (18), and replacing $n_{\mathrm{B}}$ in Eq. (21):

$$a_{\mathrm{oil}} = \frac{6\,\varepsilon_{\mathrm{oil}}}{D_{32}} \tag{23}$$

This equation allows for determining $a_{\mathrm{oil}}$ using $D_{32}$ and $\varepsilon_{\mathrm{oil}}$.

## 4. Results and discussion

It has been obtained the DSD of the emulsions indicated in Table 1. It has been calculated the polydispersity of the emul-

Table 1
Parameters of the emulsions prepared

| Oil phase concentration | Concentration of emulsifier agent | $D_{32}$ (μm) | $U$ (%) | $\varepsilon_{\mathrm{oil}}$ (cm$^3$ oil/cm$^3$ emulsion) | $10^{-2}$ $a_{\mathrm{oil}}$ (cm$^2$ oil/cm$^3$ emulsion) |
|---|---|---|---|---|---|
| Triolein, 1 wt.% | Gum arabic, 1 g/L | 2.88 | 281 | 0.0110 | 2.34 |
| Triolein, 3 wt.% | Gum arabic, 1 g/L | 3.96 | 235 | 0.0330 | 4.98 |
| | Glucopon 650, 0.2 g/L | 2.25 | 145 | 0.0330 | 14.7 |
| Triolein, 5 wt.% | Gum arabic, 1 g/L | 4.90 | 243 | 0.0549 | 5.70 |
| | Gum arabic, 3 g/L | 3.94 | 167 | 0.0549 | 8.42 |
| | Gum arabic, 5 g/L | 3.22 | 126 | 0.0549 | 10.3 |
| | Glucopon 650, 0.2 g/L | 2.49 | 244 | 0.0549 | 13.2 |
| | Findet 1214/N23, 0.2 g/L | 2.74 | 115 | 0.0549 | 12.0 |
| Tributyrin, 1 wt.% | Gum arabic, 1 g/L | 4.87 | 158 | 0.00973 | 1.20 |
| Tributyrin, 3 wt.% | Gum arabic, 1 g/L | 5.79 | 113 | 0.0291 | 3.02 |
| Tributyrin, 5 wt.% | Gum arabic, 1 g/L | 6.53 | 89 | 0.0486 | 4.47 |

sion that it is usually parameterized by the uniformity ($U$) [20] as:

$$U = \frac{1}{d_{\mathrm{v},0.5}} \frac{\sum_i V_i |d_{\mathrm{v},0.5} - d_i|}{\sum_i V_i} \tag{24}$$

where $d_{\mathrm{v},0.5}$ is the diameter for which the cumulative undersized volume fraction is equal to 50% and $V_i$ is the volume of the number of droplets existing between the two consecutive diameters. The higher $U$, the larger size distribution, given that $U$ represents the deviation from the median volume value. Mabille et al. [20] considered that an emulsion is monodisperse if $U$ is smaller than 20%. The uniformity of the emulsions prepared is shown in Tables 1 and 3. In agreement with this criterion, all the emulsions prepared are polydisperse.

$D_{32}$ and $U$ can characterize the emulsions but do not provide all the information of the emulsion. Table 1 shows the volume of the oil phase per volume of emulsion ($\varepsilon_{\mathrm{oil}}$) calculated experimentally from the oil mass used per volume of emulsion and the oil and water densities. $\varepsilon_{\mathrm{oil}}$ and $D_{32}$ are used to evaluate $a_{\mathrm{oil}}$ (Table 1).

### 4.1. Application of the equation to experimental droplet-size distributions of O/W emulsions

As example, Fig. 1A–D show cumulative $F_{\mathrm{nI}}$ versus the droplet diameter for different conditions. The models normally used to model the DSD in emulsions, normal distribution and lognormal distribution, have been applied to the experimental data but the results were unsatisfactory. The Rosin-Rammler equation, Eq. (1), has been applied to the DSD of triolein and tributyrin emulsions using $F_{\mathrm{nI}}$ instead $V_{\mathrm{cum}}$, as Bahukudumbi et al. [17] used (Eq. (2)). The integration method used was Runge-Kutta fourth order and the residual sum of squares (RSS) was calculated. The $a$ and $b$ values used to initiate the fit are between 1.2 and 5, as this author suggested. $a$, $b$ and RSS are shown in Table 2. The model fits the experimental data though the distribution of the residuals throughout the experimental range was not adequate.

Eq. (15) has also been applied to the experimental data. The $n$ and $m$ values used to begin the fit are between 0.2 and 3.5. The integration method used was Runge-Kutta fourth order and the residual sum of squares was calculated. As example,

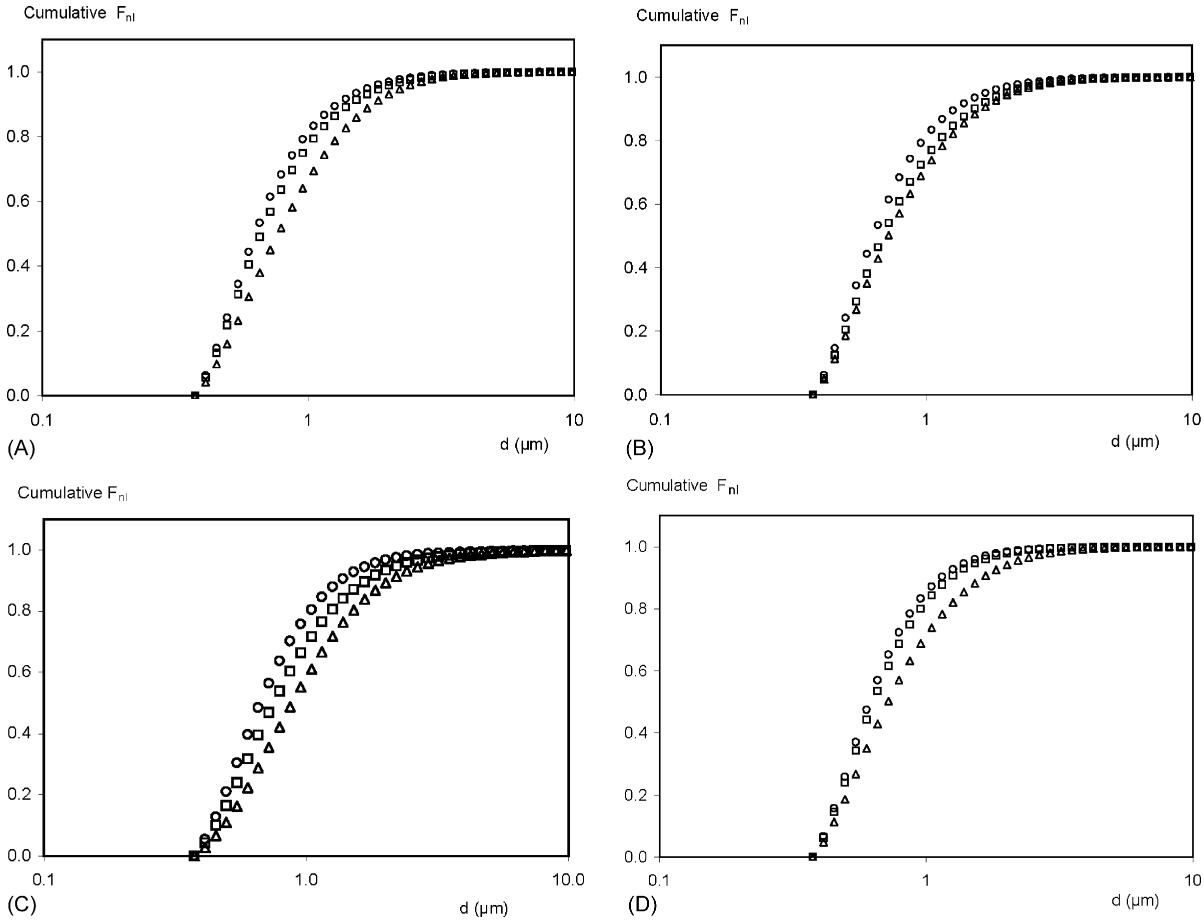

Fig. 1. DSD of triolein and tributyrin emulsions: (A) influence of the triolein concentration in 1 g/L gum arabic emulsions (△ = 1 wt.%, □ = 3 wt.%, ◯ = 5 wt.%); (B) influence of the gum arabic concentration in 5 wt.% triolein emulsions (◯ = 1 g/L, □ = 3 g/L, △ = 5 g/L); (C) influence of the tributyrin concentration in 1 g/L gum arabic emulsions (△ = 1 wt.%, □ = 3 wt.%, ◯ = 5 wt.%). (D) Influence of the aging effect in an emulsion of triolein 5 wt.%–gum arabic 5 g/L (△ = 0 min, □ = 3350 min, ◯ = 11380 min).

Table 2
Application of the Rosin-Rammler model and Eq. (15) to the experimental data

| Oil phase concentration | Concentration of emulsifier agent (g/L) | Rosin-Rammler model | | | Equation proposed (Eq. (15)) | | |
|---|---|---|---|---|---|---|---|
| | | *a* | *b* | RSS | *n* | *m* | RSS |
| Triolein, 1 wt.% | Gum arabic, 1 g/L | 0.7624 | −3.3423 | 0.058 | 1.4897 | 0.3531 | 0.00074 |
| Triolein, 3 wt.% | Gum arabic, 1 g/L | 0.8499 | −4.8687 | 0.30 | 9.6558 | 0.0796 | 0.0015 |
| | Glucopon 650, 0.2 g/L | 0.8265 | −4.2501 | 0.17 | 1.3975 | 0.3782 | 0.00035 |
| Triolein, 5 wt.% | Gum arabic, 1 g/L | 0.8871 | −6.2780 | 0.45 | 8.8902 | 0.0751 | 0.0084 |
| | Gum arabic, 3 g/L | 0.8288 | −4.3267 | 0.23 | 6.9215 | 0.1067 | 0.0014 |
| | Gum arabic, 5 g/L | 0.7991 | −3.7564 | 0.14 | 2.4946 | 0.2404 | 0.00076 |
| | Glucopon 650, 0.2 g/L | 0.8333 | −4.4054 | 0.19 | 2.0214 | 0.2959 | 0.00075 |
| | Findet 1214/N23, 0.2 g/L | 0.7910 | −3.6246 | 0.10 | 1.6979 | 0.3268 | 0.00058 |
| Tributyrin, 1 wt.% | Gum arabic, 1 g/L | 0.6759 | −2.4928 | 0.023 | 6.6559 | 0.1231 | 0.0026 |
| Tributyrin, 3 wt.% | Gum arabic, 1 g/L | 0.7787 | −3.4704 | 0.085 | 9.3429 | 0.0777 | 0.0045 |
| Tributyrin, 5 wt.% | Gum arabic, 1 g/L | 0.8730 | −5.6367 | 0.300 | 8.5458 | 0.0731 | 0.0196 |

Fig. 2A–D show that the equation reproduces satisfactorily the experimental results for the triolein and tributyrin emulsions. Table 2 shows *n*, *m* and RSS. The RSS obtained applying Eq. (15) was lesser than with the Rosin-Rammler equation independently of the oil, emulsifier agent, oil concentration and emulsifier concentration used. Table 3 shows *n*, *m* and RSS obtained when Eq. (15) is applied to the DSD of an emulsion of triolein 5 wt.% and gum arabic 5 g/L. Independently of the aging time analyzed the equation fits adequately the DSD measured. As example, Fig. 2D shows the fit of the

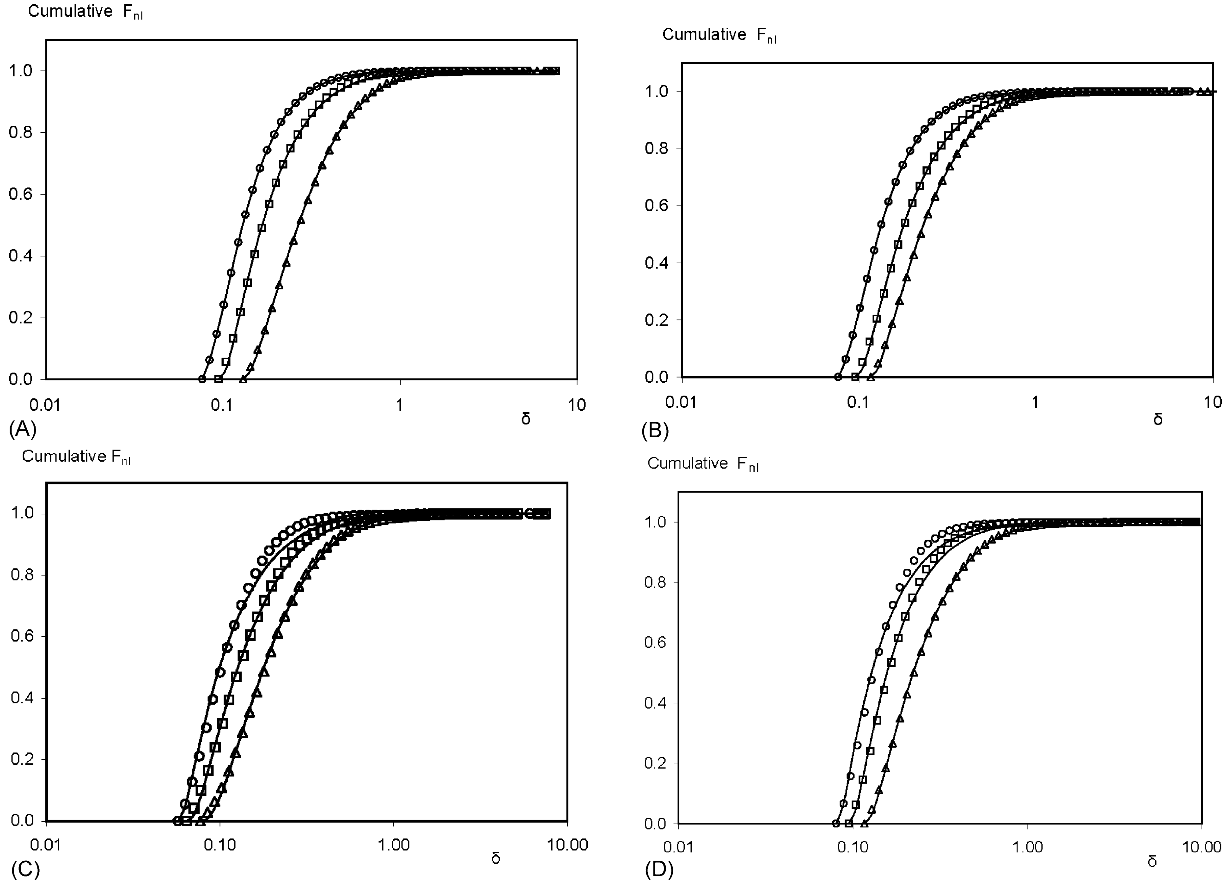

Fig. 2. Fit of Eq. (15) to the DSD of triolein and tributyrin emulsions (continuous line = simulation): (A) influence of the triolein concentration in 1 g/L gum arabic emulsions (△ = 1 wt.%, □ = 3 wt.%, ○ = 5 wt.%); (B) influence of the gum arabic concentration in 5 wt.% triolein emulsions (○ = 1 g/L, □ = 3 g/L, △ = 5 g/L); (C) influence of the tributyrin concentration in 1 g/L gum arabic emulsions (△ = 1 wt.%, □ = 3 wt.%, ○ = 5 wt.%). (D) Influence of the aging effect in an emulsion of triolein 5 wt.%–gum arabic 5 g/L (△ = 0 min, □ = 3350 min, ○ = 11380 min).

Table 3
Application of Eq. (15) to an emulsion of triolein 5 wt.%–gum arabic 5 g/L—influence of the aging effect

| Time (min) | $D_{32}$ (μm) | $U$ (%) | Equation proposed (Eq. (15)) | | |
|---|---|---|---|---|---|
| | | | $n$ | $m$ | RSS |
| 0 | 3.22 | 126 | 2.4946 | 0.2404 | 0.00076 |
| 510 | 4.04 | 105 | 6.5367 | 0.1386 | 0.0068 |
| 1280 | 4.00 | 76.3 | 9.0829 | 0.0889 | 0.0040 |
| 1710 | 4.04 | 76.3 | 9.8149 | 0.0805 | 0.0043 |
| 3350 | 3.96 | 69.7 | 9.3274 | 0.0777 | 0.0092 |
| 4330 | 4.03 | 70.0 | 9.1984 | 0.0769 | 0.0117 |
| 7220 | 4.42 | 79.5 | 8.9528 | 0.0755 | 0.0149 |
| 8530 | 4.62 | 95.8 | 8.8349 | 0.0748 | 0.0176 |
| 9980 | 4.81 | 117 | 8.7319 | 0.0742 | 0.0198 |
| 11380 | 4.67 | 71.9 | 8.7696 | 0.0744 | 0.0198 |
| 12820 | 4.92 | 81.4 | 8.6596 | 0.0738 | 0.0221 |
| 17220 | 5.16 | 75.9 | 8.5674 | 0.0732 | 0.0236 |

equation to the experimental results obtained at different aging times.

On the other hand, Eq. (23) allows for evaluating the $a_{\rm oil}$ (Table 1). As can be observed, the triolein emulsions with 1 g/L of gum arabic and different oil-phase concentration present higher $a_{\rm oil}$ values when $\varepsilon_{\rm oil}$ increases, although $D_{32}$ increases too, since there is a greater amount of oil phase in the emulsion. When the emulsions prepared with different emulsifier concentrations and 5 wt.% of triolein are compared, lower $D_{32}$ and higher $a_{\rm oil}$ are obtained when the emulsifier concentration increases.

The equation proposed has also been applied to the experimental results reported by different researchers. It has been applied to particle-size distributions of an emulsion prepared with 40% canola oil and 0.5% of the hydrocolloid gum arabic obtained by Huang et al. [21]. This emulsion was prepared emulsifying the mixture with a Polytron, and the DSD was measured at 25 °C by integrated light scattering using a Mastersizer X. Fig. 3A shows that the equation adequately fits the experimental results, so that the data can be modelled using the parameters presented in Table 4.

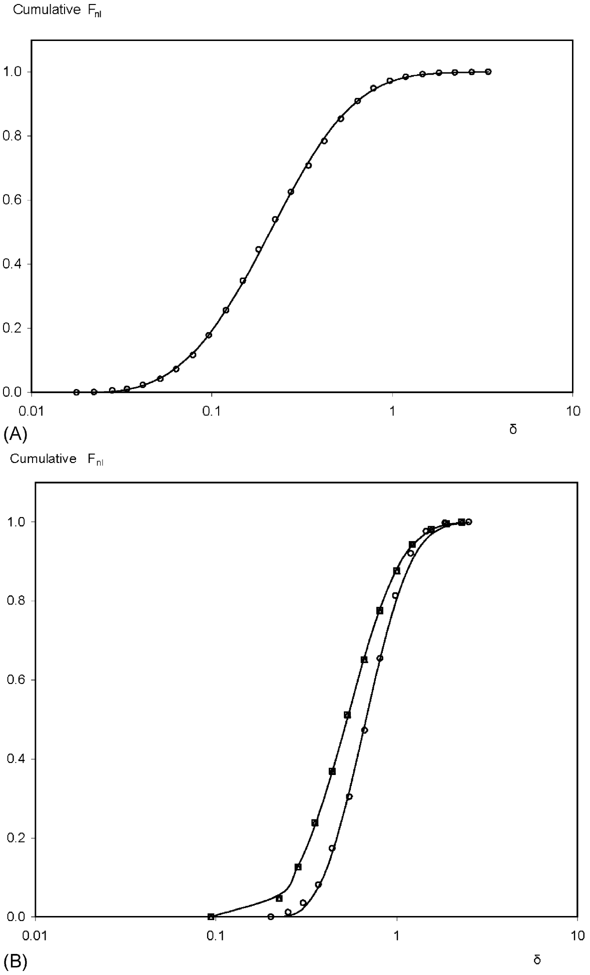

Fig. 3. Fit of Eq. (15) to the DSD of emulsions from different researchers (continuous line = simulation): (A) particle-size distributions of O/W emulsion shown in [21] (Fig. 4) (oil phase = canola oil; emulsifier agent = gum arabic); (B) particle-size distributions of O/W emulsions stabilized with whey protein without potassium chloride showed in [22] (Fig. 2). Influence of pH (○ = 5.0, □ = 6.0, △ = 6.5).

Kulmyrzaev and Schubert [22] studied the effect of pH and KCl on the stability of whey-protein-stabilized emulsions, where the protein is used as a surfactant, with 0.04 wt.% soybean O/W emulsions. The emulsions were prepared with Ultra-Turrax, and the DSD was measured using a laser scattering instrument (Mastersizer X). The equation proposed has been used to model the DSD obtained. As it is observed in Fig. 3B, the equation adequately fits the experimental results found under different experimental conditions. The parameters calculated are shown in Table 4.

On the other hand, it can be determined $F_{\rm vI}$ and $F_{\rm aI}$ by Eqs. (19) and (22) using $n$ and $m$. As example, Fig. 4A–C show $F_{\rm nI}$, $F_{\rm aI}$, and $F_{\rm vI}$ for emulsions prepared with gum arabic and triolein or tributyrin as the oil phase.

Table 4
Parameters determined applying the Eq. (15) to O/W emulsions reported by different researchers

| References | Oil phase | Emulsifier agent | $D_{32}$ (μm) | $U$ (%) | $n$ | $m$ | RSS |
|---|---|---|---|---|---|---|---|
| [21]—Fig. 4 | 40% of canola oil | 0.5% of arabic gum | 6.72 | 58 | 2.7261 | 0.3125 | 0.00062 |
| [22]—Fig. 2 | 0.04 wt.% soybean O/W emulsions | Whey protein, pH 5.0 | 25.3 | 29 | 2.4715 | 0.738 | 0.0021 |
| | | Whey protein, pH 6.0 | 0.52 | 56 | 2.6285 | 0.638 | 0.00026 |
| | | Whey protein, pH 6.5 | 1.08 | 52 | 9.1158 | 0.1595 | 0.00044 |

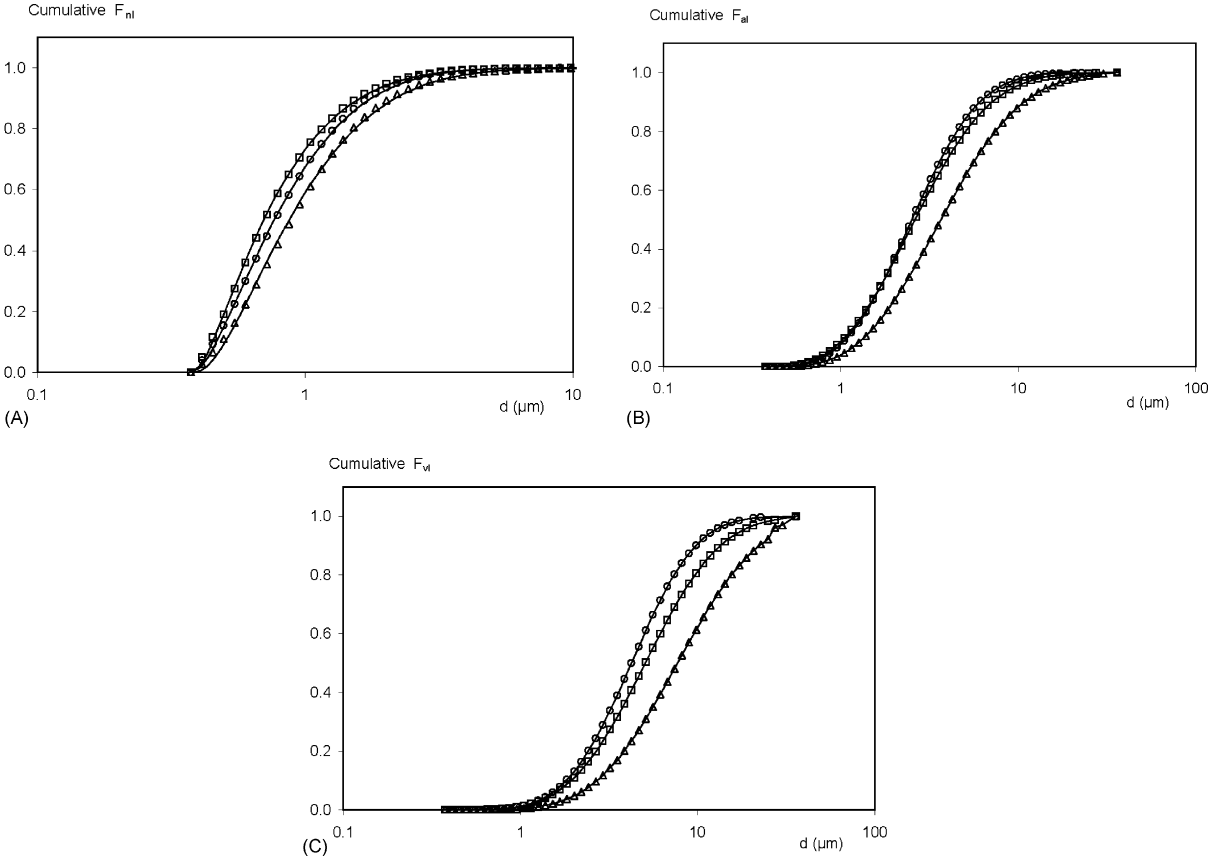

Fig. 4. Distribution functions of triolein and tributyrin emulsions (○ = 1 wt.% triolein, 1 g/L gum arabic; □ = 5 wt.% triolein, 5 g/L gum arabic; △ = 1 wt.% tributyrin; 1 g/L gum arabic): (A) $F_{\mathrm{nI}}$ (continuous line = Eq. (15) simulation); (B) $F_{\mathrm{aI}}$ (continuous line = Eq. (22) simulation); (C) $F_{\mathrm{vI}}$ (continuous line = Eq. (19) simulation).

## 5. Conclusions

The application of the equation enables to reproduce using only two parameters (*n* and *m*) the droplet-size distributions in O/W emulsions prepared with different concentrations of the oil phase (triolein and tributyrin) and different concentrations of emulsifier agents in emulsions that suffers aging effect. This equation characterize better the droplet-size distributions studied that the models used by other researchers, such as the Rosin-Rammler equation or the lognormal distribution. The *n* and *m* parameters of the equation have been estimated and they enable to model satisfactorily the droplet-size distributions reported by the authors and by different researchers. It is possible to determine too the interfacial area between the oil and water phases, a parameter of great interest in diverse chemical reactions.

This equation that has been developed is a simple and effective tool that could be used for preparing emulsions with the suitable size. It could provide greater knowledge of the behaviour of the emulsions and would be useful in different areas (engineering, pharmaceutics, biochemistry, etc.) to characterize the emulsions used, enabling precise evaluations of certain characteristics of great interest in the emulsions such as the volume-distribution function and the interfacial area distribution function.

## References

[1] H. Sis, G. Kelbaliyev, S. Chandler, Kinetics of drop breakage in stirred vessels under turbulent conditions, J. Disper. Sci. Technol. 26 (2005) 565–573.
[2] S. Sugiura, M. Nakajima, H. Ushijima, K. Yamamoto, M. Seki, Preparation characteristics of monodispersed water-in-oil emulsions using microchannel emulsification, J. Chem. Eng. Jpn. 34 (2001) 757–765.
[3] E. Fernandez, J.M. Benito, C. Pazos, J. Coca, I. Ruiz, G. Rios, Regeneration of an oil-in-water emulsion after use in an industrial copper rolling process, Colloid Surf. A-Physicochem. Eng. Asp. 263 (2005) 363–369.
[4] D.J. McClements, Food Emulsions: Principles, Practice and Techniques, CRC Press, Boca Raton, 1999.
[5] T.G. Mason, A.H. Krall, H. Gang, J. Bibette, D.A. Weitz, Encyclopedia of Emulsion Technology, Marcel Dekker, New York, 1996.
[6] P. Fernandez, V. Andre, J. Rieger, A. Kuhnle, Nano-emulsion formation by emulsion phase inversion, Colloid Surf. A-Physicochem. Eng. Asp. 251 (2004) 53–58.
[7] A. Sood, S.K. Awasthi, Initial droplet size distribution in miniemulsion polymerization, J. Appl. Polym. Sci. 88 (2003) 3058–3065.
[8] Z.D. Knezevic, S.S. Siler-Marinkovic, L.V. Mojovic, Kinetics of lipase-catalyzed hydrolysis of palm oil in lecithin/isooctane reversed micelles, Appl. Microbiol. Biotechnol. 49 (1998) 267–271.
[9] H. Polat, M. Polat, S. Chander, Kinetics of oil dispersion in the absence and presence of block copolymers, AICHE J. 45 (1999) 1866–1874.
[10] S. Sajjadi, M. Zerfa, B.W. Brooks, Dynamic behaviour of drops in oil/water/oil dispersions, Chem. Eng. Sci. 57 (2002) 663–675.
[11] M.C. Ruiz, P. Lermanda, R. Padilla, Drop size distribution in a batch mixer under breakage conditions, Hydrometallurgy 63 (2002) 65–74.
[12] A.H. Lefebvre, Atomization and Spray, Hemisphere Publishing Corporation, Washington, 1989.

[13] K.G. Hollingsworth, M.L. Johns, Measurement of emulsion droplet sizes using PFG NMR and regularization methods, J. Colloid Interface Sci. 258 (2003) 383–389.

[14] R.A. Mugele, H.D. Evans, Droplet size distribution in sprays, Ind. Eng. Chem. 43 (1951) 1317–1324.

[15] P. Angeli, G.F. Hewitt, Drop size distributions in horizontal oil–water dispersed flows, Chem. Eng. Sci. 55 (2000) 3133–3143.

[16] A.J. Karabelas, Droplet size spectra generated in turbulent pipe-flow of dilute liquid–liquid dispersions, AICHE J. 24 (1978) 170–1978.

[17] P. Bahukudumbi, K.H. Carson, A.C. Rice-Ficht, M.J. Andrews, On the diameter and size distributions of bovine serum albumin (BSA)-based microspheres, J. Microencapsul. 21 (2004) 787–803.

[18] S. Nukiyama, Y. Tanasawa, Experiments on the atomization of liquids in an air stream, Trans. Soc. Mech. Eng. 5 (1939) 62–67.

[19] N. Garti, M.E. Leser, Emulsification properties of hydrocolloids, Polym. Adv. Technol. 12 (2001) 123–135.

[20] C. Mabille, V. Schmitt, P. Gorria, F. Leal-Calderon, V. Faye, B. Deminiere, J. Bibette, Rheological and shearing conditions for the preparation of monodisperse emulsions, Langmuir 16 (2000) 422–429.

[21] X. Huang, Y. Kakuda, W. Cui, Hydrocolloids in emulsions: particle size distribution and interfacial activity, Food Hydrocolloids 15 (2001) 533–542.

[22] A.A. Kulmyrzaev, H. Schubert, Influence of KCl on the physicochemical properties of whey protein stabilized emulsions, Food Hydrocolloids 18 (2004) 13–19.