DROP SIZE DISTRIBUTION IN EMULSIONS O/W STABILIZED BY NONIONIC EMULSIFIER; DESCRIPTION OF DISTRIBUTION BY EMPIRICAL RELATIONS

Miloslav LUDVÍK[a] and Petr DURDIL[b]

[a] *Prague Institute of Chemical Technology, 166 28 Prague 6 and*
[b] *Léčiva, 109 02 Prague 10*

Received March 17th, 1982

Here is analysed how suitable are the most frequently used empirical relations for description of drop size distribution. On a representative set of emulsifying experiments is demonstrated how suitable is the three-parametric logarithmic normal distribution according to Cohen and distribution according to Espenscheid-Kerker-Matijević. For these functions are proposed methods of parameter estimation suitable for their determination from the random sample of emulsion droplets. The fittnes of testing functions is discussed briefly.

Drop size distribution in emulsion (for simplicity further on denoted as DSD), determines properties of emulsion. It is necessary to know the distribution for description of processes taking place in emulsions (formation, stability) or for description of behaviour of emulsions (rheologic properties, application characteristics *etc*). Origin of emulsions is a complicated process taking place in time with affected material properties of the system and method of preparation. At present there does not exist an all-encompassing and sufficiently physically founded theory of origin of emulsions. In this study is critically studied the suitability of the empiric relations for description of DSD in emulsions of the O/W type (oil in water).

The studies where general models of particle disintegration are considered will not be considered (Kolmogorov, Epstein, Halmos, Theimer, Troesch *etc.*) as they are too general. Mostly this concerns models based on Markovs process. Some of them were applied to emulsions[1] and confirmed validity of the log-normal distribution. Also the study by Schwarz and Bezemer[2] is not considered in which a model of emulsion formation was proposed from which results distribution of volumes of emulsion droplets. As has been demonstrated earlier[3], recalculation of the volume frequency function to the frequency function and to other usual statistical characteristics is affected by a considerable error in the region of small particles and therefore this function is generally unsuitable for description of dispersivity of emulsion. Nor the group of empiric relations for DSD at spraying of liquids is considered (Rosin-Rammler, Nikiyama-Tanasawa, Mugele-Evans *etc.*) for two reasons. Partly, they were proposed for a considerably different mechanism of droplet disintegration due to instability in the centrifugal field or pressure pulsations of the low viscosity media, partly they use the limiting droplet size (x_{max}, x_{min}). estimated from the sample. Estimation of these values, requires, as has been pointed out by Gwyn and coworkers[4], very large samples and their use for description of DSD is thus more difficult.

We are mostly interested in emulsions prepared by a mechanical stirrer of the shear type in a batch arrangement. Experiments were performed in a simple system paraffine oil-aqueous solution of nonionic emulsifier (mixed emulsifier Arlacel 80 and Tween 80-produced by Atlas, GB). Emulsions were studied in which dispersivity is not changing during emulsification (in-time-steady emulsion).

Here is considered a suitable mathematic description of DSD on a representative set of our own results and by the methods for estimation of parameters of these relations. In the second part of this study are presented the results of verification how suitable are the selected types of DSD and how their parameters change with the conditions of emulsification in the considered arrangement on an extensive set of experiments.

THEORETICAL

Selection of empirical relations for description of DSD in emulsion is determined by the positive skew of the frequency function (see further on) which is typical for the way of emulsification considered in this study. The reverse case (*i.e.* the negative skew of DSD) which is described by Rowell and Levit[5] has not been observed. Universal system of empiric frequency functions is represented by the Pearsons system (see *e.g.* the monography by Elderton and Johnson[6]). For description of DSD in emulsions of n-alkanes stabilised by yeast at fermentation[3] has resulted that the Pearsons frequency functions – type III –

$$f(x) = Y_0(1 + p_1x)^{p_2} \exp(-p_3x) , \qquad (1)$$

type X

$$f(x) = Y_0 \exp(-p_4x - 1)/p_4 , \qquad (2)$$

and type XII

$$f(x) = Y_0(p_5 - x)^{p_6} (p_7 + x)^{-p_6} \qquad (3)$$

are suitable.

In Eqs (*1*) to (*3*) is Y_0 the normalizing factor and p_1 to p_7 are distribution parameters, which can be determined from moment equations[6]. In these relations and further on is x the size of the droplet and $f(x)$ the frequency function.

Another suitable type with regard to its skewness is the log-normal distribution. Contrary to the two-parametric distribution[1,7,10] defined on a whole set of values $\{x\}$ here is considered physically most acceptable three-parameter distribution, which is proposed *e.g.* by Cohen[8] in the form

$$f(x) = [\gamma(x - \alpha) \sqrt{(2\pi)}]^{-1} \exp\{-\ln^2 [(x - \alpha)/\beta]/2\gamma^2\} . \qquad (4)$$

In relation (4) are α, β, γ parameters with following significance: α is the minimum size of the droplet, β logarithmic mean, γ logarithmic standard deviation. The frequency function is defined for $x \geqq \alpha$ which is in agreement with the basical knowledge on disintegration of droplets in an emulsion. Cohen reports on procedure for estimate of parameters by the method of maximum likelihood. This procedure enables to estimate α and thus also the minimum size of droplets from the shape of frequency data which could be useful when this interesting characteristics of emulsions is studied. The momentum estimate of parameters in a somewhat modified log-normal distribution

$$f(x) = [\gamma(x - \alpha)\sqrt{(2\pi)}]^{-1} \exp\{-[\ln(x - \alpha) - \beta]^2/2\gamma^2\} \tag{5}$$

is presented by Wicksell[9]. The detailed description of properties of the log-normal distribution can be found in the monography by Aitchinson and Brown[10].

The distribution by Espenscheid–Kerker–Matijević[11] is also considered, which is for simplicity denoted as EKM distribution

$$f(x) = \frac{x^n \exp[-(\ln x - \ln \bar{x}_1)^2/2\sigma_1^2]}{\sqrt{(2\pi)}\,\sigma_1 \bar{x}_1^{n+1} \exp[(n+1)^2 \sigma_1^2/2]}, \tag{6}$$

where n, $\bar{x}_1$ and σ_1 are distribution parameters (see later on).

Parameters are in the quoted study[11] fitted simultaneously by computer minimalisation of the squared deviation of the empirical and calculated dependence of DSD. This procedure has been modified in this study. Rowell and Levit[5] proposed for description of DSD in emulsions two relations: skewed normal distribution (SND)

$$f(x) = \frac{1 - s^2}{\sigma\sqrt{(2\pi)}} \exp\left\{-\frac{[x - x_M - s|x - x_M|]^2}{2\sigma^2}\right\} \tag{7}$$

and skewed zeroth-order logarithmic distribution (SZOLD)

$$f(x) = \frac{|s|}{\sigma x_M \sqrt{(2\pi)} \exp(\sigma^2/2)} \exp\left\{\frac{\ln^2[1 + s(x - x_M)/x_M]}{2\sigma^2}\right\}. \tag{8}$$

In relations (7) and (8) appear three parameters: skew s, breadth σ and modus x_M. The authors[5] do not consider their estimate.

In all mentioned relations is $f(x)$ the frequency function of droplet sizes. It can be compared with the experimental frequency function defined for the grouped distribution of frequencies by relation

$$f_e(x) = n_i/(\Delta x_i \sum_i n_i), \tag{9}$$

where n_i is the frequency in the i-th interval of sizes, Δx_i is the width of this interval and $N = \sum_i n_i$ is the sample size.

Knowledge of this function enables to calculate also the surface frequency function $f_a(x)$ or the volumetric function $f_v(x)$ which are sometimes used in the analysis of properties of emulsions[2,12] and which are defined by relations

$$f_a(x) = n_i x_i^2 / (\Delta x_i \sum_i n_i x_i^2), \quad (10a)$$

or

$$f_v(x) = n_i x_i^3 / (\Delta x_i \sum_i n_i x_i^3). \quad (10b)$$

RESULTS AND DISCUSSION

For the characteristic set of experimental data discrimination of the discussed DSD types was made. This set enclosed 12 emulsifying experiments and was chosen so that basical variables have varied in the maximum range: impeller speed n_M = = 1 000 to 1 750 min^{-1}, volumetric concentration of oil in emulsion x_{vd} = 2 to 10 vol.%, volumetric concentration of emulsifier x_{ve} = 0·1 to 0·5 vol.%. Basical characteristics of the used drop samples and experimental conditions are given in Table I.

TABLE I

Emulsification conditions and characteristics of droplet samples

Experiment	Emulsification conditions			Characteristics of sample						
	n_M / min^{-1}	x_{vd} / vol.%	x_{ve} / vol.%	N	μ_1 / µm	x_M / µm	σ / µm	γ_1	γ_2	$\bar{x}_{32}$ / µm
1	1 000	5	0·2	547	14·30	5·43	13·75	1·644	2·311	38·91
2	1 250	5	0·2	531	11·84	4·67	10·94	1·738	2·375	31·50
3	1 500	3	0·2	792	10·99	5·04	8·468	1·315	1·046	23·33
4	1 500	3	0·5	936	6·177	2·82	5·720	2·930	13·12	19·62
5	1 500	5	0·1	761	6·010	2·50	6·265	3·234	12·70	22·82
6	1 500	5	0·2	589	7·219	3·32	5·932	2·776	8·088	19·68
7	1 500	5	0·5	680	8·534	3·71	7·367	1·751	2·601	21·33
8	1 500	10	0·2	936	6·089	2·73	5·760	2·949	10·24	19·86
9	1 500	10	0·5	993	7·315	3·62	5·542	2·601	9·538	17·91
10	1 750	5	0·2	613	6·624	3·05	4·707	9·827	42·76	15·52
11	1 750	5	0·5	677	8·849	3·66	7·891	6·286	17·25	21·97
12	1 750	10	0·5	757	6·539	2·86	6·795	6·795	25·42	21·33

The experiments and their evaluation is described in detail in the following study. Suitability of the individual types of the Pearson frequency function system can be evaluated *e.g.* by the moment criteria proposed by Elderton and Johnson[6], which are not fulfilled for the data considered in this study for the types III, X and XII. *E.g.* for the measurement No 8 (Table I) the conditions are for type III

$$2\beta_2 \neq 6 + 3\beta_1 \,, \tag{11}$$

and for type XII

$$5\beta_2 - 6\beta_1 - 9 \neq 0 \,. \tag{12}$$

Here $\beta_1 = m_3^2/m_2^3 = 2{\cdot}694$ and $\beta_2 = m_4/m_2^2 = 12{\cdot}93$ are ratios of powers of central moments of r-th order m_r.

Out of DSD types proposed by Rowell and Levit[5] for the sets studied here is more suitable SZOLD (see Eq. (*8*)). From the parameters x_M – modus of distribution has the clear significance (the most frequent value). Parameter has been considered the logarithmic variance and s the skew parameter, fitted according to the criteria of best fittness of the empiric and calculated DSD. As an example can be given the shape of DSD in Fig. 1 according to relations (*7*) and (*8*) for the experiment No 12. In this case following values were used: $x_M = 3{\cdot}1$ μm, $\sigma = 0{\cdot}7034$ μm and $s = 1{\cdot}25$ (for SZOLD) and $s = 0{\cdot}83$ (for SND). The dependence SZOLD is satisfactory, SND is in agreement with the empirical function in the mode but its skew is not suitable. Disadvantage of the function SZOLD is its limited definition interval with regard to allowed values of logarithm in the exponential. It is obvious that there must hold

$$x > x_M(s - 1)/s \,. \tag{13}$$

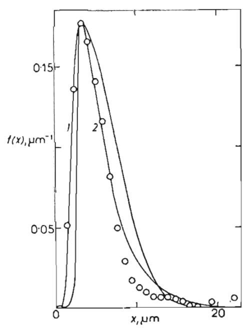

FIG. 1

Frequency functions according to Rowell and Levit[5]. ○ experimental values (Exp. No 12); *1* SZOLD according to Eq. (*8*); *2* SND acaccording to Eq. (*7*)

For the function given in Fig. 1 this condition has the form $x > 0{\cdot}62\ \mu m$. It is obvious that the conditions (*13*) can be in contradiction with the minimum droplet size given by physical conditions of emulsification and is thus generally unsuitable.

From the given two relations for lognormal distribution (see Eqs (*4*) and (*5*)) the relation by Cohen[8] has been selected with regard to the more suitable method of parameter estimation (the authenticity method of maximum likelihood). The shape of function given by Eq. (*5*) with parameters estimated by the moment method proposed by Wicksell[9] is not satisfactory for reasons given in the discussion of results.

Lognormal distribution according to Cohen[8]. The estimate function for parameter α was arranged for grouped frequencies into the form

$$\lambda(\alpha) = [\sum_i n_i/(x_i - \alpha)]\,\{N \sum_i n_i \ln(x_i - \alpha) - N \sum_i n_i \ln^2(x_i - \alpha) + [\sum_i n_i \ln(x_i - \alpha)]^2\} - N^2 \sum_i [n_i \ln(x_i - \alpha)/(x_i - \alpha)]\,, \qquad (14)$$

where N was the sample size.

Summations in relation (*14*) are made for all clases of grouped frequencies sought. The sought estimate of parameter α is the root of equation

$$\lambda(\alpha) = 0 \qquad (15)$$

which was solved by the iteration Newton method with the tolerance $1\,.\,10^{-4}$. The iteration relation has the form

$$\alpha^{(j)} = \alpha^{(j-1)} - \lambda(\alpha^{(j-1)})/\lambda'(\alpha^{(j-1)})\,, \qquad (16)$$

where $\lambda'(\alpha)$ is the derivative according to parameter determined by relation

$$\lambda'(\alpha) = \left(\sum_i \frac{n_i}{(x_i - \alpha)^2}\right) \{N \sum_i n_i \ln(x_i - \alpha) - N \sum_i n_i \ln^2(x_i - \alpha) + [\sum_i n_i \ln(x_i - \alpha)]^2\} + \sum_i \frac{n_i}{x_i - \alpha} \left\{2N \sum_i \frac{n_i \ln(x_i - \alpha)}{x_i - \alpha} - N \sum_i \frac{n_i}{x_i - \alpha} - 2 \sum_i \frac{n_i}{x_i - \alpha} \sum_i n_i \ln(x_i - \alpha)\right\} - N^2 \left[\sum_i \frac{n_i \ln(x_i - \alpha)}{(x_i - \alpha)^2} - \sum_i \frac{n_i}{(x_i - \alpha)^2}\right]. \qquad (17)$$

At localisation of roots of Eq. (*15*) it was necessary to start from the differing course of the estimate function $\lambda(\alpha)$ which had for some data in the first interval of value x_1 (numerically $x_1 = 0.4$ μm) a discontinuity (see Fig. 2*a*). In this case or in the case when $\alpha > x_1$ (see Fig. 2*b* – points denoted by full circle) the summations in relations (*14*) and (*17*) are limited from bottom by the value $i = 2$ and the root of Eq. (*15*) was sought between x_1 and x_2. The shape of function $\lambda(\alpha)$ in Fig. 2*b* (values denoted by empty points) represent the normal case which has occurred with majority of treated experiments.

The parameters β and γ are given by relations

$$\ln \beta = (1/N) \sum_i n_i \ln (x_i - \alpha), \quad (18a)$$

$$\gamma^2 = (1/N) \sum_i n_i \ln^2 (x_i - \alpha) - [(1/N) \sum_i n_i \ln (x_i - \alpha)]^2. \quad (18b)$$

EKM *distribution*. With regard to another method of fitting parameters of DSD (from optical measurements for very fine emulsions and zóles) the quoted authors[11] have not considered their estimates from the random samples of drops. From the position of maximum of function (*6*) it is possible to derive the relation for parameter

$$n = 2(\ln x_M - \ln \bar{x}_1), \quad (19)$$

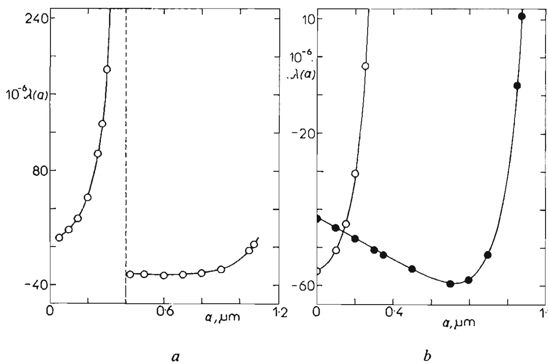

FIG. 2

Dependence of the estimated function for parameter α in Eq. (*4*). *a* Dependence with discontinuity *b* continuous dependences where

$$\ln \bar{x}_1 = (1/N) \sum_i (n_i \ln x_i) \tag{20}$$

is the logarithmic mean of distribution, and x_M is the modus. The remaining parameter is given by the usual relation for the logarithmic standard deviation

$$\sigma_1^2 = (1/N) \sum_i n_i(\ln x_i - \ln \bar{x}_1)^2 . \tag{21}$$

At determination of x_M value it was decided to use the numerical procedure starting from the empirical frequency function. The modus was localized according to the change of sign of the first derivative of this function calculated from the differenceless Lagrange formula for seven initial points. The value of the mode determined as the maximum on the second degree polynomial calculated by the least square method in vicinity of maximum $f_e(x)$ is distorted (mostly increased) with regard to asymmetry of DSD. It was taken only as the first trial $x_M^{(0)}$ into the numerical solution which was based on minimalisation of the sum of square deviations of the experimental and theoretical frequency functions

$$\Delta^2 = \sum_{i=1}^{k} [f(x_i) - f_e(x_i)]^2 . \tag{22}$$

The characteristic dependences Δ^2 with the mode, which affects $f(x_i)$ over the parameter n (see Eqs (*15*) and (*16*)), are plotted in Fig. 3. The value of x_M or of parameter n according to Eq. (*19*) was determined by the Aitken interpolation in the table of derivatives of function Δ^2 according to x_M for the zero value of derivative (condition for minimum). The minimum was sought with the step 0·1 μm on both sides of the first trial $x_M^{(0)}$ so that the accuracy of about $1 \cdot 10^{-3}$ was reached at interpolation of the mode.

The agreement of experimental and calculated DSD is considered according to the two most frequently used goodness of fit tests[14] – Pearson's χ^2 test

$$\chi^2 = \sum_{i=1}^{k_g} (n_i - n_{ie})/n_i , \tag{23}$$

where n_i is the interval frequency according to calculated DSD, n_{ie} is the experimental interval frequency and k_g is the number of classes of droplet sizes arranged by grouping so as to suit the requirements on statistical significance. The second one is the Smirnov's test

$$D_n = \sup_x |F(x) - F_e(x)| , \tag{24}$$

where $F(x)$ and $F_e(x)$ are the calculated and experimental distribution functions which are determined numerically from tables of frequency functions.

As the additional criteria, values of the average absolute deviation of frequency functions are given

$$\delta = 100 \sum_{i=1}^{k} |f(x_i) - f_e(x_i)|/k\,. \tag{25}$$

From characteristics of selected sets are given the values which quantify in a certain way form of empirical frequency functions and so the possibility to describe them by the chosen DSD type. This is the usually used average μ_1 (first moment) modus x_M and standard deviation σ (square root of second central moment).

Moreover the skewness is given

$$\gamma_1 = \mu_3/\sigma^3\,, \tag{26}$$

where μ_3 is the third moment and coefficient of peakness $\gamma_2 = \mu_4/\sigma^2 - 3$, where μ_4 is the fourth moment.

The last given moment characteristics is the Sauter's mean

$$\bar{x}_{32} = \mu_3/\mu_2\,. \tag{27}$$

Results achieved by verification of relations other than Eqs (*4*) and (*6*) were discussed in the preceeding part of this study. Conditions of emulsification experiments are given in Table I together with basic characteristics of drop samples. Determined values of parameters for both studied functions defined by Eqs (*4*) and (*6*) are given in Tables II and III together with values of goodness of fit tests and their critical values.

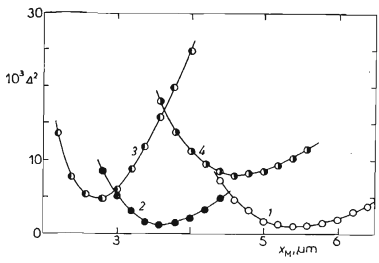

FIG. 3

Dependence of quadratic deviation Δ^2 according to Eq. (*22*). *1* Exp. No 1; *2* exp. No 9; *3* exp. No 8; *4* exp. No 2

TABLE II

Parameters of log-normal distribution according to Cohen[8] and goodness of fit. Critical values χ^2_{cr} are read from published tables[13] for 95% confidence. Critical 95% value $D_{n,cr}$ = 1·356 for all given sets

Experimental	Parameters				Goodness of fit criteria			
	α	β	γ	δ	χ^2	k_g	χ^2_{cr}	D_n
1	0·699	8·352	1·030	0·3340	53·9	29	38·9	0·634
2	0·191	8·200	0·811	1·0750	127	24	32·7	2·180
3	0·364	7·810	0·817	0·3885	93·9	25	33·9	0·932
4	0·820	3·541	0·933	0·4247	25·8	23	31·4	0·805
5	0·055	4·278	0·774	0·6529	0·65	21	30·1	1·780
6	1·127	4·547	0·727	0·7513	59·1	17	23·7	1·385
7	0·662	5·385	0·891	0·3675	48·5	24	32·7	0·632
8	0·015	4·583	0·725	0·771	79·1	21	30·1	1·570
9	0·588	5·202	0·721	0·3286	29·6	23	31·4	0·557
10	0·071	5·474	0·578	0·5818	37·0	17	23·7	0·650
11	0·013	5·275	0·824	1·2210	135	23	31·4	2·005
12	0·800	3·837	0·873	0·9780	115	27·6	27·6	1·540

TABLE III

Parameters of distribution according to Espenscheid–Kerker–Matijević[11] and goodness of fit. Values of χ^2_{cr} are read from published tables[13] for 95% confidence. Critical 95% value $D_{n,cr}$ = = 1·356 for all sets

Experimental	Parameters			Goodness of fit criteria				
	n	χ_1	σ_1^2	δ	χ^2	k_g	χ^2_{cr}	D_n
1	−1·107	2·246	0·845	0·4298	74·7	28	37·7	1·167
2	−1·184	2·134	0·621	1·0168	159	23	21·4	1·812
3	−0·971	2·110	0·624	0·4186	88·3	25	33·9	0·811
4	−0·953	1·513	0·617	0·5586	55·6	24	32·7	1·657
5	−1·037	1·470	0·580	0·6368	52·1	21	30·1	1·613
6	−1·096	1·770	0·358	0·9264	87·7	17	23·7	1·429
7	−1·053	1·835	0·616	0·4457	64·6	23	31·4	0·728
8	−1·037	1·526	0·521	0·7022	93·7	21	30·1	1·056
9	−0·972	1·773	0·433	0·4116	33·1	23	31·4	0·889
10	−1·146	1·715	0·324	0·5901	49·7	17	23·7	0·766
11	−1·086	1·849	0·675	1·1875	164	23	31·4	1·995
12	−1·073	1·588	0·495	1·0529	179	—	26·3	2·247

Agreement of the calculated DSD with empirical functions can be also judged from the graphs where experimental values are denoted by circles.

Generally speaking the fittness of log-normal and EKM distributions can be considered good without regard to the shape of function $f_e(x)$. Description of sets with different asymmetry coefficients does not cause any problems with Eqs (*4*) and (*6*) as expected. Preliminary considerations demonstrated that the fittness was good with sets both with low values of the peakness coefficient – measurement No 1 and 3 for $\gamma_2 = 2{\cdot}311$ and $\gamma_2 = 1{\cdot}046$ as well as with high values of $\gamma_2 = 13{\cdot}12$ and $\gamma_2 = 12{\cdot}70$ for the measurements No 4 and 5. Greater deviations of calculated functions from experimental values for measurements No 2 and 11 are due to second local maximum on the curve $f_e(x)$ in the region 10–15 μm which cannot be described by the tested functions. This question is discussed in detail in the following paper. The priority region of better fittness of individual functions on this investigation level have not been found.

The fittness is judged quantitatively by comparison of the calculated and critical values of goofness of fit criteria (see Eqs (*23*) and (*24*)). The test according to Eq. (*24*) is in 50% of the studied cases positive, while the test according to Eq. (*23*) is positive only in two cases out of twelve. To judge these results would require a more thorough analysis which is not done here with regard to the nature of this study. It is possible

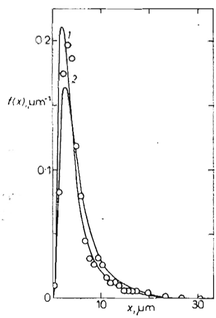

FIG. 4

Frequency function according to Eqs (*4*) and (*6*) plotted through the experimental points – exp. No 5 *1* EKM distribution according to Eq. (*6*); *2* log-normal distribution according to Eq. (*4*)

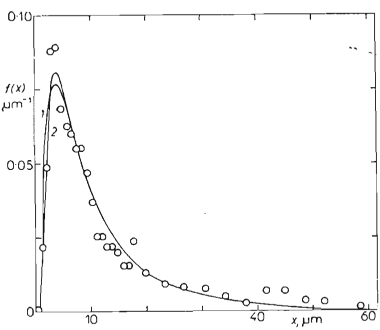

FIG. 5

Frequency function according to Eq. (*4*) and (*6*) plotted through the experimental points– experiment No 1 *1* EKM of distribution according to Eq. (*6*); *2* log-normal distribution according to Eq. (*4*) to say that the goodness of fit tests according to the χ^2 criteria can be considered only as an orientation with regard to the "weight" of deviations which makes more pronounced deviations at the ends of distributions and thus also in the region of mentioned second local maxima.

It is possible to conclude, that both types of frequency functions – log-normal according to Cohen (Eq. (*4*)) and according to Espenscheid–Kerker–Matijević (Eq. (*6*)) are suitable for description of droplet size distribution of the emulsion of the type O/W stabilised by nonionic emulsifier. The proposed algorithm of the parameter estimation have proved successful and thus this investigation can be extended to a larger range of emulsification experiments.

LIST OF SYMBOLS

D_n	Smirnov criteria of goodness of fit
$F(x)$	drop size distribution function
$f(x)$	drop size frequency function (μm^{-1})
k_g	number of grouped classes of droplet sizes
m_r	r-th central moment (μm^r)
N	sample size
n	distribution parameter in Eq. (*6*)
n_i	frequency in i-th size interval
n_M	impeller speed (min^{-1})
p_1 to p_7	parameters of Pearson's functions in Eqs (*1*) to (*3*)
s	skew parameter in Eqs (*7*) and (*8*)
x	droplet size (μm)
x_{vd}	volume fraction of oil (%)
x_{ve}	volume fraction of emulsifier (%)
$\bar{x}_{32}$	Sauter mean (μm)
$\bar{x}_1$	logarithmic mean in Eq. (*6*), defined by Eq. (*20*) (μm)
x_M	modus (most frequently size) of droplet (μm)
Y_0	normalizing factor in Eqs (*1*) to (*3*)
α	parameter of log-normal distribution in Eqs (*4*) and (*5*)
β	parameter of log-normal distribution in Eqs (*4*) and (*5*)
β_1, β_2	moment characteristics according to Pearson
γ	parameter of log-normal distribution in Eqs (b) and (*5*)
γ_1	skew coefficient, Eq. (*26*)
γ_2	peakness coefficient, Eq. (*27*)
Δ^2	summary quadratic deviation, Eq. (*22*)
Δx_i	width of i-th interval of droplet sizes (μm)
δ	mean absolute deviation, Eq. (*25*)
$\lambda(\alpha)$	estimate function according to Eq. (*14*)
μ_r	r-th initial moment (μm^r)
σ	standard deviation droplet sizes (μm)
σ_1	logarithmic standard deviation in Eq. (*6*). defined by Eq. (*21*) (μm)
χ^2	Pearson's goodness of fit

REFERENCES

1. Rajagopal E. S.: Kolloid-Z. Z. Polym. *162*, 85 (1959).
2. Schwarz N., Bezemer C.: Kolloid-Z. Z. Polym. *146*, 139 (1956).
3. Ludvík M., Prokop A.: This Journal *40*, 52 (1975).
4. Gwyn J. E., Crosby E. J., Marshall W. K. jr: Ind. Eng. Chem. Fundam. *4*, 204 (1965).
5. Rowell R. L., Levit A. B.: Colloid Interface Sci. *53*, 340 (1975).
6. Elderton W. P., Johnson L. P.: *Systems of Frequency Curves*. University Press, Cambridge 1969.
7. Gebelein H.: Mitteilungsbl. Math. Statistik (München) *1950*, 155.
8. Cohen A. C. jr: J. Amer. Statist. Assoc. *46*, 206 (1951).
9. Wicksell S. D.: Ark. Mat. Astr. Fysik *12*, 1 (1971).
10. Aitchison J., Brown J. A. C.: *The Lognormal Distribution Function*. Univesity Press, Cambridge 1957.
11. Espenscheid W. F., Kerker M., Matijević E.: J. Phys. Chem. *68*, 3093 (1964).
12. Djaković Lj., Dokić P., Radivojević P., Kler V.: Colloid Polym. Sci. *254*, 907 (1976).
13. Janko J.: *Statistické tabulky*. Academia, Prague 1958.
14. Walsh J. E.: *Handbook of Nonparametric Statistics*. van Nostrand, Princeton (Vol. I) 1962, (Vol. II) 1965.

Translated by M. Rylek.