DROP SIZE AND DROP SIZE DISTRIBUTION IN A LIQUID-LIQUID EXTRACTION SPRAY COLUMN

Muhammad Tariq Saeed, M. Jamil and E.S. Perez De Ortiz*

PCSIR Laboratories Complex, Shahrah-e-Jalaluddin Roomi, Lahore-54600, Pakistan

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A photographic method was used for the estimation of drop size and drop size distribution obtained from multiple nozzles for a chemical system (zinc/di(2-ethylhexyl) phosphoric acid) for solute transfer from continuous to dispersed and dispersed to continuous phase. The experiments were performed in a glass spray column under semi-batch operation. Experimentally obtained drop sizes were compared with those predicted from drop size correlations for jetting and non-jetting conditions and the ones predicting best results are given for design purposes.

Key words: Drop formation, Mass transfer, Photographic method, Metal extraction.

Introduction

Knowledge of the interfacial area between droplets and continuous phase is required for the design of continuous counter-current contactors in which droplets of a liquid are passed through another partially or totally immiscible liquid. Interfacial area is important in heat and mass transfer processes and is a function of drop size and dispersed phase holdup or volume fraction.

The size of a drop formed in an immiscible liquid is dependent upon the physical properties of the system and the formation conditions. Drop formation has been studied by many investigators and theoretical or empirical correlations for drop size have been proposed, although disagreement between various expressions is substantial. In most of the cases, drops were formed at single nozzle submerged in a quiescent continuous liquid.

Most of these developed correlations were tested with mutually saturated phases. It was predicted [1,2] drop size correctly for physical systems where mass transfer was occuring. The objective of this paper is to check the validity of drop size correlations to chemical system, i.e. zinc/di(2-ethylhexyl) phosphoric acid system.

Drop size correlations. When a dispersed phase is passed through a nozzle immersed in an immiscible continuous phase, the most important parameters influencing the resultant drop size are interfacial tension, nozzle diameter, the velocity of dispersed phase through nozzle, viscosity and density of continuous phase and density and viscosity of dispersed phase. In general, an increase in interfacial tension, continuous phase viscosity and nozzle diameter increase the drop size whereas the increase in density difference between phases results in its decrease. The correlation for the formation of drops at low nozzle velocities (non-jetting region) from a

* Department of Chemical Engineering, Imperial College, London SW7, UK.

single nozzle and swarms of drops from a set of nozzles or perforated plates are available in the literature [1-12]. The calculation of drop size, by using the correlations of Scheele and Meister [1] , Hayworth and Treybal [3], and de Chazal and Ryan [7], is iterative as they contain the drop volume term on both sides. The Scheele and Meister correlation becomes simple when the continuous phase viscosity is less than 1×10^{-3} P_a s since the drag term is then negligible. The correlation of de Chazal and Ryan [7] is complex because it requires the terminal velocity, u_t, which is a function of the drop size. Terminal velocity can be calculated from the correlations of Hu and Kintner [13] and Klee and Treybal [14].

The correlations of Scheele and Meister [1] and de Chazal and Ryan [7] also contain the Harkins and Brown's correction factor, accounting for the drop fraction remaining at the nozzle when the drop detaches. This factor was originally replotted by Scheele and Meister [1]. Heertjes *et al.* [8] presented a plot for ψ_H as a function of the properties of system. According to de Chazal and Ryan [7], a value of 0.625 can be used for most practical solutions. However, Horvath et al. [15] derived the following approximate equation by using the graph published by Scheele and Meister [1].

$$\psi_H = 0.6 + 0.4 \exp(-2x) \qquad \text{............................ (1)}$$

where

$$X = d_n \left\{ \frac{\Delta \rho g}{\pi \sigma d_n} \right\}^{1/3} \qquad \text{............................. (2)}$$

The drop size correlations mentioned above are applicable for drop formation (single drop region) directly at a set of nozzles or orifices in a perforated plate when no liquid jet is formed. The liquid filament connecting meniscus and main droplet depends upon the velocity of dispersed phase through the nozzle. In order to distinguish between non-jetting and

jetting regions of drop formation, minimum jetting velocity at which jet formation begins is required which can be evaluated from the existing correlations [7, 16-19]. Drop formation under different external forces was first studied by Rayleigh in 1882 and correlations predicting the drop diameter under jetting conditions have been developed by several workers [2,12,15,20-27].

Experimental

Reagents. The continuous aqueous phase contains zinc sulphate, sodium sulphate and sulphuric acid whereas the dispersed phase consists of di (2-ethylhexyl) phosphoric acid in n-heptane. The zinc sulphate, sodium sulphate and sulphuric acid used were of analytical reagent grade. The n-heptane supplied by Shell Company was of knock-testing grade and was used without further purification. The di(2-ethylhexyl) phosphoric acid (DEHPA) was of technical grade and was purified according to the method of Partridge and Jensen [28]. Table 1 gives the physical properties of the system studied.

Procedure. Experiments were performed in a glass spray column of 1.55m effective height and 0.05m diameter (Fig. 1). The dispersed phase was introduced through 4 nozzles situated at the base of the column. The drops were formed on sharp
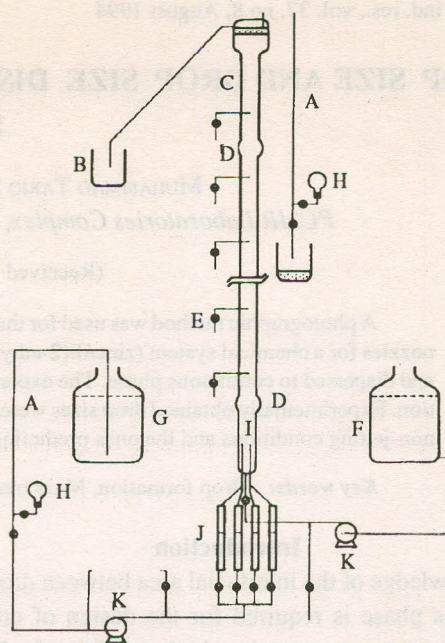

Fig. 1. Schematic flow diagram of the experimental apparatus. A. Siphon, B. Overflow, C. Column, D. Plane glass windows, E. Sampling tube, F. Continuous phase reservoir, G. Dispersed phase reservoir, H. Siphon starter (Pipette filler), I. Nozzles, J. Rotameters, K. Magnetically driven centrifugal pumps.

TABLE 1. PHYSICAL PROPERTIES OF THE SYSTEM STUDIED.

AQUEOUS PHASE:

$$ZnSO_4 + Na_2SO_4 + H_2SO_4 + H_2O \text{ for extraction experiments.}$$
$$Na_2SO_4 + H_2SO_4 + H_2O \text{ for stripping experiments.}$$

ORGANIC PHASE:

  n-heptane + DEHPA for extraction experiments.
  n-heptane + DEHPA + Zinc-DEHPA complex for extraction and stripping experiments.

TEMPERATURE = 25°C

Aqueous phase Kmol/m³	Organic phase kmol/m³	ρ_c kg/m³ (10³)	ρ_d kg/m³ (10³)	μ_c kg/ms (10⁻³)	μ_d kg/ms (10⁻³)	$\sigma\ddagger \pm 0.5$ N/m (10⁻³)
I = 0.3 $C_{zt} = 1.59 \times 10^{-3} -$ 4.37 x 10⁻³ pH = 2.36-3.07	$C_{oD} = 0.075$ $C_{zo} = 0$	1.01	0.695	0.9524	0.4733	20.5
I = 1, pH = 2.4-3.07 $C_{zt} = 1.57 \times 10^{-3} - 0.20$	$C_{oD} = 0.075$ $C_{zo} = 0$	1.04	0.695	1.0225	0.4733	20.5
I = 1, pH = 2.7-3 $C_{zt} = 0.01-0.02$	$C_{oD} = 0.025$ $C_{zo} = 0$	1.04	0.685	1.0225	0.4365	22.5
I = 1, $C_{zot} = 0$ pH = 1.5-1.65	$C_{oD} = 0.075$ $C_{zo} \sim 0.065$	1.04	0.717	1.0225	0.53	18
I = 1, pH = 2.7 $C_{zt} = 3.5 \times 10^{-3}$	$C_{oD} = 0.075$ $C_{zo} \sim 0.103$	1.04	0.729	1.0225	0.6025	18

‡ Average values for the conditions given in the first column.

edged glass capillary nozzles. The four nozzles were located on the corners of a square. Three different nozzle sets were used as given elsewhere [29]. The nozzle tips were immersed in the stationary continuous phase, contained in the column. The flow rate through the nozzles can be measured and controlled individually. Two flat windows, one at the top and the other at the bottom, allow for the dispersion to be photographed with a cine camera. The column was operated in a semi-batch mode, i.e. the continuous aqueous was kept stagnant and the dispersed phase was not recirculated. Full details of the apparatus description and photographic setup is given elsewhere [29,30].

Results and Discussion

Drop size measurement. The dispersion was photographed at two locations along the column height, i.e. 0.14 and 0.9m from the nozzle. The film clearly showed the presence of shape oscillation, wobbling and zig-zag motion of the drops (Fig. 2). Observed shape oscillations were of the spherical oblate type. An Optomax Image Analyzer (Analytical Measuring Systems, U.K.) was used employing the standard software and interface for the measurement of major and minor axes of drops from the photographic film for different runs. The scale on the film was used as a reference. In order to simplify the measurement, the drops are assumed to be perfect ellipsoids. The equivalent diameter of single drops, $'d_e$, and the Sauter mean diameter, d_{32}, of the dispersion were calculated by using standard equations [31,32], namely:

$$'d_e = \sqrt[3]{d_1^2\, d_2} \quad\text{...}(3)$$

$$d_{32} \quad \frac{\Sigma\, n\, 'd_e^3}{\Sigma\, n\, 'd_e^2} \quad\text{...}(4)$$
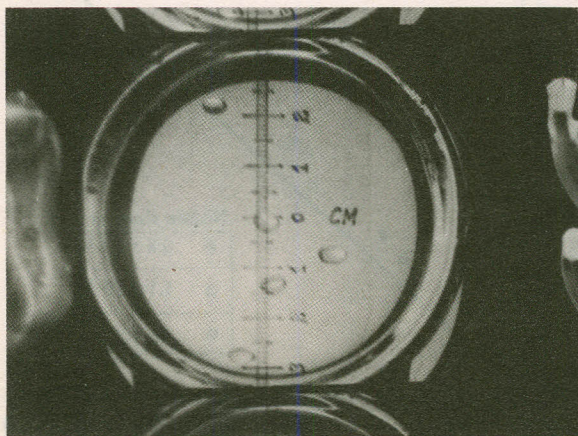

Fig. 2. Typical photograph of dispersion in the column.
d_n = 1.1 mm, $'L_d$ = 10.5 ml/min., d_e = 5.04 mm (extraction experiments). Photograph taken at 14 cm from nozzle tips.

where d_1 and d_2 are the horizontal and vertical axis lengths of the drops and n is the number of drops of diameter $'d_e$.

Drop size distribution. Drop size distribution is important in heat transfer, mass transfer and chemical reactions in liquid-liquid systems. Also the behaviour of single representative drop is not enough to describe this phenomena when a drop size distribution is present. So it is desirable to measure drop size distribution in a liquid-liquid extraction column.

Drop size distribution implies more accurate method for the determination of each droplet fraction in the dispersion. In order to make a comparison between the values of experimental and predicted drop size from drop size correlations (available in the published literature), the average equivalent drop diameter of the dispersion was estimated from drop size distribution measured at two different heights, i.e. 0.14 and 0.9m, by a photographic method. To keep the dispersed phase holdup at a low level, and thereby to minimize the possibility of coalescence and other multiple drop interactions, low flow rates were used.

Comparison between experimental and predicted drop sizes. There are many theoretical and empirical correlations for determination of size of the drop formed at a single nozzle and at a set of nozzles or orifices in a perforated plate. Unfortunately, inspite of these extensive investigations, the correlations show areas of disagreement and the expression presented by one investigator often fails to fit the experimental data obtained by another.

To find the correlation which gives the best prediction of drop size for the system under study for jetting and non-jetting conditions, several correlations were examined and some of them were compared with experimental data as shown in Fig. 3 and 4. The values of various physical properties needed in the calculations were determined experimentally. It should be noted that the drops were observed to form at the outside diameter of nozzles in the non-jetting region. The inner and outer diameters were used as appropriate when applying the drop size correlations.

Under non-jetting conditions, the correlations proposed earlier [1 - 3] gave better results (Fig. 3a, 3b and 3c). Comparing the experimental drop sizes with those predicted by these correlations, the average deviation is 4, 7 and 9% respectively. Rest of the correlations gave unsatisfactory approximations to the experimental results.

Using the calculated values of Harkins and Brown's correction factor from equation (1), which in turn corresponds to the graph published in Scheele and Meister's work [1], the correlations of Scheele and Meister [1] and de Chazal and Ryan [7] gave large deviations whereas the value of 0.625 recommended by de Chazal and Ryan [7] predicted better results as

Table 2. Comparison of Measured Drop Sizes with Predicted Values Using Different Values of ψ_H under Non-Jetting Conditions for Extraction Experiments.

Nozzle type	L'_d m³/s (10^-8)	d_e m (10^-3)	d_{32} m (10^-3)	Predicted drop size (10^-3)m			
				Ref No. (1)		Ref No. (7)	
				ψ_H	ψ_H	ψ_H	ψ_H
				0.625	‡	0.625	‡
A	9.17	3.99	3.99	4.39	4.78	4.65	5.06
	11.17	3.68	3.68	4.36	4.75	4.39	4.89
B	10.83	5.22	5.25	5.4	5.81	6.21	6.57
	12.5	5	5.04	5.4	5.82	6.32	6.68
	17.5	4.94	5	5.39	5.8	6.39	6.78
C	24.17	6.28	6.31	6.29	6.48	7.23	7.38
	33.33	6.23	6.25	6.36	6.55	7.67	7.81
	50	6.07	6.09	6.45	6.65	8.39	8.51

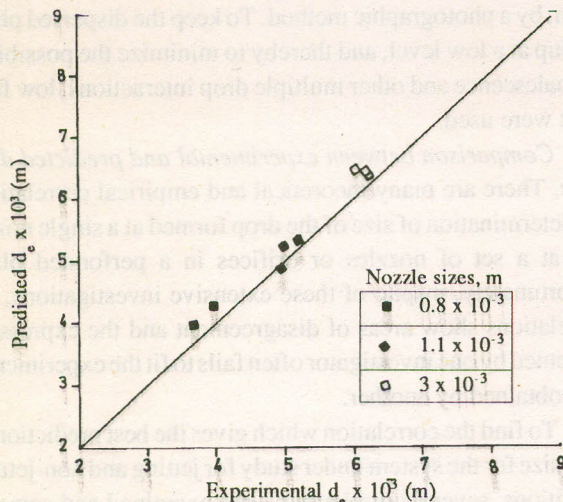‡ Values of ψ_H calculated from equation (1).

Fig. 3a. Comparison of experimental and predicted d_e values from Hayworth and Treybal's correlation [3] for non-jetting region.
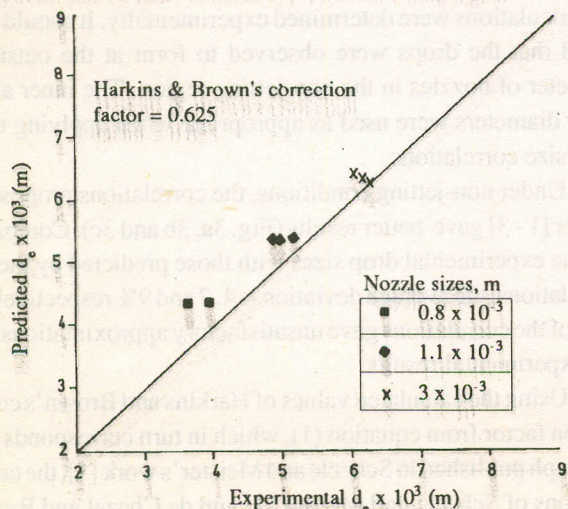

Fig. 3b. Comparison of experimental and predicted d_e values from Scheele and Meister's correlation [1] for non-jetting region.

shown in Table 2. The terminal velocity in de Chazal and Ryan's correlation was calculated from the Klee and Treybal's correlation [14]. Almost identical values were obtained using Hu and Kintner's relationship [13].

Under jetting conditions, the experimental data was well fitted by the correlations of Kumar and Hartland [2], Kumar [27] an Hayworth and Treybal [3] as shown in Figs 4a and 4b with and average deviation of 5, 6 and 5% respectively. Various workers [15,22,24-27] have developed correlation between jet and droplet diameters. The jet diameter is a function of physical properties of the system used. In the correlations of Meister and Schelee, Skell and coworkers, Horvath et al. and Kumar, the jet diameter was calculated using the jet diameter at breakup suggested by Skell and and Huang [26].

Effect of mass transfer direction on drop size. To ascertain the influence of mass transfer direction on the drop size, experiments were also conducted with zinc transferring from the dispersed to the continuous phase.

A comparison is shown in Figs. 4a and 4b between experimental and predicted drop sizes from correlations for the stripping of zinc-DEHPA complexes in *n*-heptane with acidic aqueous solutions, i.e. mass transfer from dispersed to continuous phase (d → c direction) in this study. It is seen in this figure that drop size correlations are not adequate to predict the experimental drop sizes. On the other hand, there is a good agreement between experimental and predicted drop sizes from the correlations for extraction experiments, i.e. mass transfer from the continuous to the dispersed phase (c → d direction), as shown in Figs. 4a and 4b.
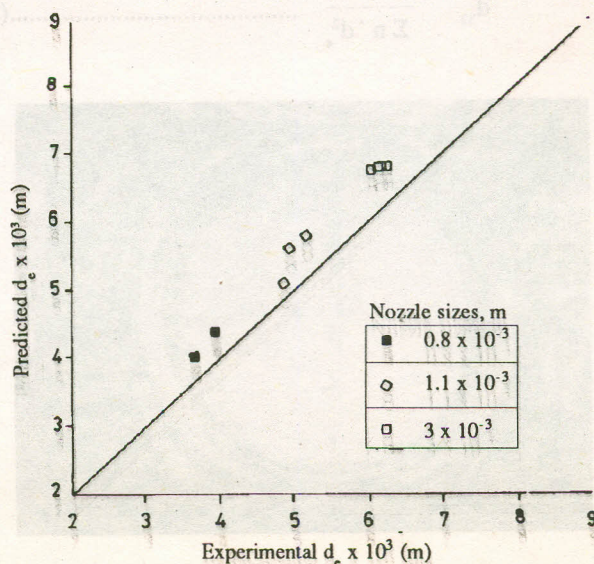

Fig. 3c. Comparison of experimental and predicted d_e values from Kumar and Hartland's correlation [2] for non-jetting region.

The difference between the two mass transfer directions can then be interpreted in terms of the different coalescence behaviour in the two directions of transfer. The presence of a solute tends to lower the interfacial tension ($d\partial/dC < 0$) between two immiscible liquids [33-35]. When one phase is dispersed in the other and mass transfer occurs from continuous to dispersed phase, concentration of solute in draining film between two approaching drops is lower than the bulk concentration of surrounding continuous phase so that local interfacial tension is greater and drainage of the liquid film is retarded. Consequently, coalescence of the drops is inhibited.
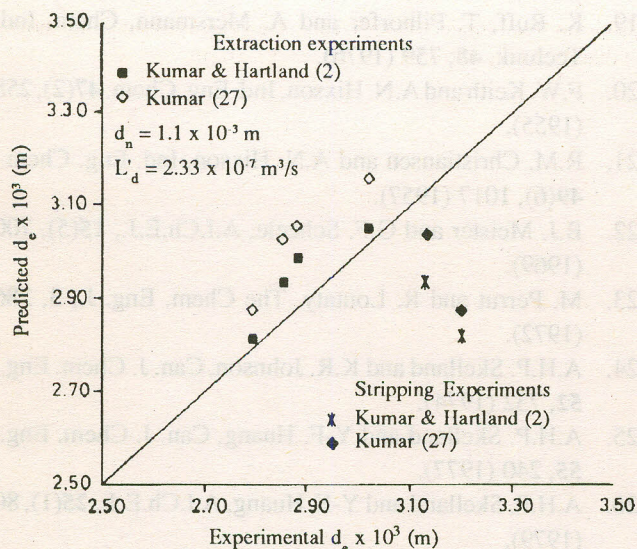

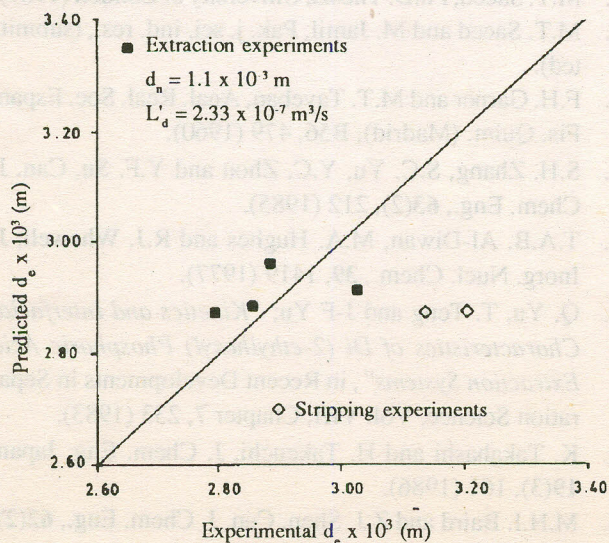Fig. 4a. Comparison of experimental and predicted d_e values for jetting region.

Fig. 4b. Comparison of experimental and predicted d_e values from Hayworth & Treybal's correlation (3) for jetting region.

On the other hand, when mass transfer occurs from dispersed to continuous phase, concentration of the solute in the film between two adjacent drops is greater than the bulk concentration of continuous phase. Hence, the local interfacial tension is lowered, drainage of liquid film separating the drops is accelerated and coalescence of the drops is promoted. This phenomenon is usually called Marangoni thin film effect.

A similar explanation could be proposed for the zinc/DEHPA system. In this system, extraction of zinc from aqueous phase decreases the concentration of DEHPA at the interface. This leads to an increase in ∂ thus preventing drop coalescence. However, the reverse is true for stripping, i.e. the reaction increases the interfacial DEHPA concentration with the consequent decrease in ∂. Under these conditions drop coalescence is promoted.

For mass transfer from continuous to dispersed phase (extraction experiments) even in the jetting region, drop coalescence was not observed in the column proper. Drops collided but each drop kept its own identity. Hence, good agreement was obtained between experimental values and predictions by the drop size correlations. However, for mass transfer in the opposite direction (stripping experiments), the drop coalescence took place in the column proper as can be inferred from the photographs [29]. There was also evidence from the visual observation of the column that some drops coalesced during their rise in the column. It may be possible for drop size to be governed by conditions during its formation when mass transfer takes place. Mass transfer does not affect characteristics of drop formation but affects mainly physical properties of the system which in turn affects the drop size. The drop size in $d \rightarrow c$ mass transfer direction was greater than that in the opposite direction, i.e. $c \rightarrow d$ mass transfer direction. This is consistent with the findings of different workers [32, 36, 37] who have reported that when mass transfer direction is from dispersed phase to continuous phase, droplet coalescence in their system studies leads to larger drops.

Conclusion

Drop size of the dispersion in a spray column for a chemical system (zinc/d; (2-ethylhexyl) phosphoric acid) was measured using a photographic method.

Under non-jetting conditions, the correlation proposed by Scheele and Meister [1] and Kumar and Hartland [2] for drop sizes gave good results with an average absolute deviations of 7 and 9% respectively for extraction experiments.

Under jetting conditions, the experimental results of drop sizes were well fitted by the correlation of Kumar and Hartland [2] for extraction experiments whereas this correlation is inadequate to predict the experimental drop sizes for stripping experiments. The correlation of Hayworth and Tre-

bal [3] can also be used for the prediction of drop size both for jetting and non-jetting conditions.

The drop sizes formed for extraction experiments were smaller than those for stripping experiments.

NOMENCLATURE

(The SI system is used throughout this paper)

C	=	Molar concentration
d_1	=	Major axis of ellipsoid
d_2	=	Minor axis of ellipsoid
d_{32}	=	Sauter mean drop diameter
d_e	=	Equivalent diameter of the dispersion
d_e	=	Equivalent drop diameter of single drops
d_n	=	Nozzle diameter
g	=	Acceleration due to gravity
I	=	Ionic strength
L'_d	=	Dispersed phase flow rate per nozzle
n	=	Number of drops in the dispersion
u_t	=	Terminal velocity of drops

GREEK LETTERS

$\Delta \rho$	=	Density difference between phases
∂	=	Interfacial tension
ψ_H	=	Harkins-Brown correction factor
ρ_c	=	Continuous phase density
ρ_d	=	Dispersed phase density
μ_c	=	Continuous phase viscosity
μ_d	=	dispersed phase viscosity

SUBSCRIPTS

o	=	DEHPA dimer
zO	=	Organic phase zinc
zt	=	Total aqueous phase zinc

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