

THE VOLUME OF A DROP AT FINITE RATE OF FORMATION

K. GRIGAR, J. PROCHÁZKA and J. LANDAU

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchbát*

Received March 4th, 1971

The dependence was examined of the volume of a drop on the velocity of the dispersed phase in the nozzle, the diameter of the nozzle and physical parameters of the system. 8 systems were investigated. The thus far published relationships were compared and the constants of a simple relation proposed in this paper were evaluated on the basis of the experimental results obtained.

In the paper^{1,2} we have examined the pressure loss at formation of a drop in one of the openings of a sieve plate. This paper deals with the dependence of the volume of the drop on the velocity in the nozzle, the diameter of the nozzle and the parameters of the system.

The first attempt to derive a relationship for the volume of a drop under quasi-static conditions was made by Traube³. At later date Lohnstein⁴ carried out analysis on the basis of the Laplace-Young equation and derived a relation for the maximum volume of a pendant drop. By means of a simple assumption he calculated the volume of the liquid left at the nozzle tip and hereby the volume after break-off. He introduced coefficient Φ into Traube's relation representing a correction on the volume of the residual liquid adhered to the nozzle and on the fact that the surface line does not generally make the right angle with the plane of the nozzle opening.

$$V = (\pi/2) \Phi da^2. \quad (1)$$

A greater accuracy has been achieved by Harkins and Brown⁵ by determining the dependence $\Phi(\tilde{r})$, or $\Phi(r/V^{1/3})$, from experimental data. One of the first papers to deal with the drop formation at non-zero velocity in the nozzle is that of Hayworth and Treybal⁶. The authors proposed a relationship based on Eq. (1) in which an average value of $\Phi = 0.655$ is used. The volume at quasi-static formation is corrected on the effect of friction, V_1 , and the effect of momentum inflow, V_2 :

$$V = V_s + V_1 - V_2. \quad (2)$$

Ueyama⁷ started from Eq. (2) but for the calculation of V_s he used $\Phi(\tilde{r})$ given by Harkins and Brown. For V_1 the author proposed two relations valid for lower respectively higher values of the viscosity of continuous phase. For the correction on momentum effect, V_2 , he also proposed two relations depending whether the diameter of the drop is smaller or greater than that of the nozzle. Null and Johnson^{8,9} proposed also a solution based on simplified geometrical models of the drop before reaching equilibrium and in the course of break-away. From analysis of pictures they concluded that further growth occurs during necking. Similar approach was

adopted by Rao and coworkers¹⁰. An empirical relation for the dimensionless volume of the drop, $\tilde{V} = V/a^3$, as a function of \tilde{r} and w in a graphical form was proposed by Siemes^{11,12}. As a formal drawback of this correlation appears that the velocity was not expressed in dimensionless form.

Scheele and Meister¹³ assume equilibrium of the forces acting on the drop at the instant of the drop break-away. A correction on the increase of the volume during necking, V_3 , is also introduced. In contrast to the relationship of Hayworth and Treybal, where Φ appears as a factor only in the expression for V_s , Φ factors the whole right hand side of the resulting relation. If the effect of individual forces is expressed by appropriate corrections of the volume, the resulting relation is as follows

$$V = \Phi(V_s + V_1 - V_2 + V_3). \quad (3)$$

Thus it is assumed that at finite rate of formation the pendant drop breaks into the separated drop and the rest clinging to the tip of the nozzle in the same way as at quasi-static formation. The relationships of Scheele and Meister represent the so far most detailed analysis of the process of drop formation at finite rates. Since their equations contain three empirical constants and simplifying assumptions were used for their derivation, it seems justified to propose a simpler relation of empirical nature preserving the structure of Eq. (3).

THEORETICAL

The volume of a drop is generally a function of physical properties of the liquid system, the diameter of the nozzle and the velocity in the nozzle. From physical properties significant effect exerts the interfacial tension and the densities of both phases. Viscosity is important only in the range of greater values and its effect will not be considered. The velocity profile at discharge from the nozzle may affect the momentum transfer into the drop within 30% of its mean value. The effect on the volume of the drop is substantially smaller. Under these assumptions we thus have

$$V = V(w, d, \rho_D, \rho_C, g, \sigma) \quad (4)$$

and in dimensionless form

$$\tilde{V} = \tilde{V}(We, \tilde{d}). \quad (5)$$

In accord with the results of Scheele and Meister¹² the function (5) was expressed as a polynomial in We

$$\tilde{V} = a_0(\tilde{d}) + a_1(\tilde{d}) We^{1/3} + a_2(\tilde{d}) We^{1/2} + a_3(\tilde{d}) We. \quad (6)$$

The first term on the right hand side possesses the meaning of the static volume. Following relation was obtained from the data of Lohnstein¹

$$a_0(\tilde{d}) = 1.042\tilde{d}^{-0.118}, \quad 0 < \tilde{d} < 2.4. \quad (7)$$

The second term represents a correction on the increase of volume during break-away.

The third term corresponds to a correction on the action of friction forces. The value of $1/2$ of the exponent of We is based on assumption of purely viscous friction. In such a case a_2 should be proportional to μ_C . For a low value of viscosity this term should be small; for prevailing inertia losses the exponent would become equal unity and the third term would coincide with the second one. The fourth term corresponds to a correction on the momentum transfer. From the above follows that the coefficients a_0 through a_2 should be positive, a_3 negative.

To facilitate optimization of the functions $a_1(\bar{d})$, $a_2(\bar{d})$, $a_3(\bar{d})$ for the set of data from Experimental of this paper, the following form, which is sufficiently flexible and enabling easy processing, was chosen for Eq. (6):

$$\bar{V} = 1.042\bar{d}^{-0.118} + \bar{d}^m [A We\bar{d}^n + B(We\bar{d}^n)^{1/2} + C(We\bar{d}^n)^{1/3}], \quad (8)$$

where A , B , C , m , n , are empirical constants.

EXPERIMENTAL

A detailed description of the apparatus has been published earlier^{1,2}. The drops were originated at constant velocity in the nozzle. The flow rate of the dispersed phase was determined by weighing the volume discharged during a certain period. A photo-electric counter was used to count the drops. The water phase was always dispersed. The nozzles were made of brass with the edges bevelled at an angle of 5° to prevent wetting of the outer surface of the nozzle. For the same reason the outer surface was coated with teflon in some cases. A total of 8 liquid systems were studied. Their properties are summarized in Table I. Table II comprises the diameters of the nozzles used for measurement in individual systems. The correlation proceeded in several steps: In the first step the values of the exponents n and m were searched so as to obtain best fit of the experimental

TABLE I
Physical Properties of the Systems (CGS)

System	Dispersed phase	Continuous phase	ρ_D	ρ_C	σ	a	μ_D	μ_C
1	Water	petrol-tetrachloromethane	0.9982	1.3334	38.6	0.484	0.010	0.0068
2	Water	tetrachloromethane	0.9982	1.5943	43.0	0.384	0.010	0.0091
3	Water	petrol-tetrachloromethane	0.9982	1.0497	34.0	1.160	0.010	0.0051
4	Water	chlorobenzene	0.9982	1.1059	37.0	0.836	0.010	0.0040
5	Water	petrol	0.9982	0.7130	28.0	0.447	0.010	0.0056
6	Water	toluene	0.9982	0.8630	33.0	0.705	0.010	0.0056
7	Water-glycerol	toluene	1.1960	0.8630	22.5	0.372	0.373	0.0056
8	Water	paraffin oil	0.9982	0.8880	47.4	0.937	0.010	0.5190

Measured at 20°C .

points in $(\bar{V} - 1.042\bar{d}^{-0.118})/\bar{d}^m$ versus $(We\bar{d}^n)$ plot. Having found suitable values of these exponents ($n = -1, m = 0.5$) the group $(\bar{V} - 1.042\bar{d}^{-0.118})\bar{d}^{-0.5}$ was correlated as a dependent variable with (We/\bar{d}) as an independent variable by the least square method. All experimental points (except for $w = 0$) of the systems 2-4, 6 were used in the correlation (239 points altogether) and the following values of the coefficients were obtained:

$$A = 0.00465, \quad B = -2.103, \quad C = 2.657; \quad \sigma = 0.0917.$$

This corresponds to the final equation

$$V = a^2 d \{ 1.042 \bar{d}^{-0.118} + \bar{d}^{0.5} [0.00465 (We/\bar{d}) - 2.103 (We/\bar{d})^{0.5} + 2.657 (We/\bar{d})^{1/3}] \}, \quad \text{for } 0 < \bar{d} < 2.4. \quad (9)$$

The values of V_C were calculated from this equation for all measurements of this work. The average relative error of all measurements with respect to the correlation in Eq. (9) is 11.2%. The selection of four systems out of the total of eight for determining the values of the constants was made in an attempt to evaluate the constants from the data which undoubtedly satisfy the assumptions of the relation. Thus the systems 7 and 8 with high viscosity of continuous or dispersed phase were omitted. The systems 1 and 5 were omitted as being suspected of surface active agent contamination.

DISCUSSION

The values of the constants of Eq. (9) obtained by correlation do not meet the expectations following from comparison with the relation of Scheele and Meister¹³. A whole series of combinations of numerical values of the exponents of We were tested systematically but the combination appearing in Eq. (8), or (9) displayed the minimum variance. From the common correlation conspicuously deviate only the

TABLE II

Values of the Dimensionless Diameter \bar{d} for Nozzles Used for Measurements of Individual Systems

System	0.108	0.148	0.199	0.249	0.300	0.351	0.401
1	—	—	—	—	0.610	—	—
2	0.282	0.386	0.518	0.648	0.780	0.914	1.042
3	—	—	0.172	—	0.258	—	0.346
4	—	0.176	0.238	0.298	0.358	0.420	—
5	—	—	0.446	0.558	—	0.786	—
6	—	—	0.282	0.354	—	0.498	—
7	—	—	0.534	0.670	—	0.944	—
8	—	—	0.212	0.266	—	0.374	—

data of the water-petrol system. The cause may be the presence of impurities in technical petrol since also the changes of interfacial tension with time were observed here. An interesting finding is that conspicuous deviations are exhibited neither by the system aqueous solution of glycerol-toluene with higher viscosity of the dispersed phase, nor by the water-paraffin oil system with higher viscosity of the continuous phase.

While Eq. (9) can be rearranged into the form of a function of one independent variable (We/\bar{d}), this cannot be done with the relations of other authors. Consequently, a direct graphical comparison cannot be made except for a definite system and diameter of the nozzle. Fig. 1 gives such comparison for the water-tetrachloromethane system. In this case the curve corresponding to Eq. (9) is very close to that

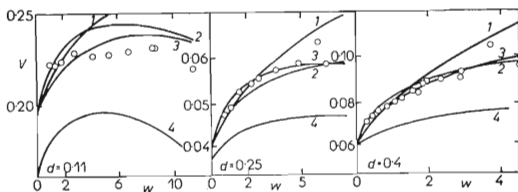


FIG. 1

Comparison of Different Relationships for the Volume of the Drop with Experimental Results in System 2

1 Scheele and Meister¹³; 2 Equation (9); 3 Ueyama⁷; 4 Hayworth⁶.

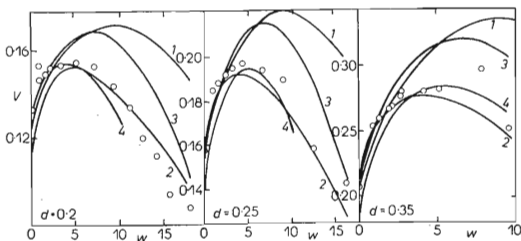


FIG. 2

Comparison of Different Relationships for the Volume of the Drop with Experimental Results in System 6

given by Ueyama⁷ and both agree well with the results of measurement. The other two relations deviate distinctly at higher velocities. Fig. 2 shows in a similar fashion the relations and the experimental data for the water-toluene system. In this case the curve of Eq. (9) and that by Hayworth and Treybal⁶ approximate each other.

TABLE III

Comparison of the Relations on the Basis of the Average Relative Error of Experimental Measurements of this Work

System	d	N	Eq. (9)	Scheele ¹²	Ueyama ¹⁷	Siemes ¹¹	Hayworth ^{6 a}
1	0-30	37	0-083	0-114	0-063	0-133	0-227
2	0-11	11	0-064	0-101	0-053	0-088	0-185
	0-15	9	0-087	0-109	0-087	0-112	0-204
	0-20	10	0-052	0-080	0-042	0-057	0-193
	0-25	12	0-048	0-073	0-049	0-080	0-217
	0-30	14	0-060	0-090	0-038	0-072	0-172
	0-35	12	0-039	0-065	0-026	0-079	0-195
	0-40	20	0-052	0-076	0-045	0-096	0-227
3	0-20	21	0-173	0-108	0-080	0-215	0-078
	0-30	17	0-113	0-111	0-121	0-192	0-056
	0-40	24	0-088	0-086	0-112	0-218	0-107
4	0-15	24	0-129	0-258	0-210	0-142	0-080
	0-20	13	0-110	0-221	0-185	0-159	0-080
	0-25	15	0-081	0-230	0-178	0-151	0-084
	0-30	17	0-082	0-227	0-191	0-127	0-108
	0-35	10	0-072	0-173	0-152	0-086	0-104
5	0-20	12	0-195	0-134	0-151	0-272	0-318
	0-25	11	0-261	0-159	0-198	0-315	0-346
	0-35	10	0-264	0-142	0-180	0-297	0-371
6	0-20	13	0-064	0-216	0-137	0-166	0-123
	0-25	11	0-049	0-136	0-075	0-158	0-103
	0-35	11	0-045	0-098	0-081	0-146	0-065
7	0-20	14	0-088	0-078	0-162	0-061	0-058
	0-25	17	0-155	0-073	0-177	0-101	0-145
	0-35	13	0-085	0-056	0-148	0-117	0-092
8	0-20	13	0-096	0-121	0-200	0-196	0-329
	0-25	12	0-068	0-125	0-216	0-176	0-321
	0-35	12	0-073	0-096	0-218	0-174	0-306
		415	0-112	0-141	0-131	0-162	0-195

^a Only the experimental points from the range $0 \leq w \leq 10$ (352 points) compared.

TABLE IV
Comparison of the Relations on the Basis of the Average Relative Error of Measurements of Different Authors

System	<i>N</i>	<i>d</i>	Eq. (9)	Scheele ¹²	Ueyama ⁷	Hayworth ⁶
Methyl isobutyl ketone-water (Null)	68	0.169	0.141	0.256	0.186	0.468
	42	0.207	0.105	0.250	0.143	0.456
	42	0.248	0.123	0.223	0.151	0.424
	39	0.261	0.070	0.196	0.128	0.420
	38	0.312	0.143	0.123	0.077	0.358
	36	0.331	0.160	0.125	0.072	0.319
	32	0.460	0.082	0.136	0.107	0.257
Benzene-water (Null)	20	0.201	0.393	0.537	0.412	0.517
	20	0.252	0.105	0.334	0.099	0.101
	29	0.261	0.098	0.262	0.152	0.156
	34	0.312	0.095	0.272	0.150	0.173
	30	0.331	0.270	0.117	0.198	0.084
	29	0.460	0.099	0.199	0.100	0.124
Water-benzene (Null)	20	0.260	0.206	0.419	0.246	0.136
	20	0.358	0.109	0.323	0.201	0.134
Ethyl acetate-water (Null)	20	0.269	0.486	0.537	0.559	0.807
	20	0.305	0.430	0.471	0.506	0.774
Cotton oil-water (Null)	17	0.263	0.325	0.107	0.329	0.133
	18	0.314	0.293	0.163	0.400	0.190
Water-cotton oil (Null)	20	0.260	0.260	0.387	0.514	0.697
	20	0.358	0.366	0.457	0.606	0.787
Water-tetrachloromethane (Null)	15	0.270	0.307	0.098	0.425	0.417
	19	0.348	0.543	0.091	0.632	0.555
Tetrachloromethane-water (Null)	19	0.280	0.943	0.336	1.129	1.051
Water-tetrachloromethane (Siemes)	12	0.100	0.151	0.263	0.119	0.285
	11	0.200	0.083	0.209	0.123	0.210
	9	0.300	0.227	0.171	0.447	0.266
	13	0.400	0.234	0.149	0.254	0.443
	10	0.600	0.170	0.153	0.083	0.529
Heptane-water (Scheele)	7	0.254	0.287	0.064	0.347	0.225
Heptane-glycerol (Scheele)	7	0.081	1.359	0.533	0.144	0.453
Butanol-water (Scheele)	8	0.081	0.190	0.221	0.306	0.859
Tetrachloromethane + heptane- water (Scheele)	19	0.254	0.202	0.114	0.114	0.297

A general comparison of Eq. (9) with equations of other authors using our set of data is presented in Table III containing the average relative errors for subsets corresponding to individual systems and nozzle diameters. It is seen that the relation (9) fits best. Only the results for the velocity in the nozzle $w \leq 10$ cm/s were taken into calculation from the relation of Hayworth and Treybal since the authors restrict its validity to this region. It may be expected that the empirical relation will exhibit the best agreement for the set from which its constants were evaluated. Accordingly, the comparison was also made with experimental results of other authors. Table IV gives the results of measurements taken from three papers^{9,10,13}, together with the values calculated from Eq. (9). The wide range of the drop volumes covered (three orders of magnitude) and the fact that no systematic deviation appears in any particular region strengthens the credibility of appropriateness of our relation.

This impression is further corroborated by the fact that for some groups of points displaying greater deviations the authors report values of the interfacial tension considerably different from those given in the literature. The use of the value from the literature would improve the agreement altogether. This is the case of, for instance, the system water-tetrachloromethane and water-petrol in the work of Null. Conspicuously deviate the data of Scheele and Meister for the heptane-glycerol system. The cause might be that Eq. (9) is not suitable for systems with high viscosity of the continuous phase. It seems also that systematically deviate the data for small nozzle diameters.

A greater part of measurements of Null and of Scheele and Meister were carried out under conditions when the dispersed phase is the one which does not wet the wall of the nozzle. According to our experience the reproducibility of such measurements is lower than in the opposite case (if the above mentioned precautions regarding the bevel angle of the nozzle and teflon coating are observed).

As it is further seen the sets which deviate conspicuously from Eq. (9), deviate usually from other relations too. The variance of majority of sets with respect to any of the relations is greater on average than that of the data of this work. From this observation it may be concluded that a significant source of deviations from Eq. (9) is the inaccuracy of measurements.

LIST OF SYMBOLS

a	$(2\sigma/\Delta\rho g)^{1/2}$	capillary constant (L)
d		diameter of nozzle (L)
\tilde{d}	d/a	dimensionless diameter of nozzle
D		diameter of drop (L)
N		number of experimental points
Q		volumetric flow rate in nozzle (L^3T^{-1})
r		radius of nozzle (L)
\tilde{r}	r/a	dimensionless radius of nozzle
V		volume of drop (L^3)

V_s	volume of drop at quasi-static formation (L^3)
V_1	friction correction of volume (L^3)
V_2	correction of volume of drop on momentum of inflowing liquid (L^3)
V_3	correction of volume of drop on inflow during necking (L^3)
$\bar{V} = V/(a^2d)$	dimensionless volume of drop
w	average linear velocity of liquid in nozzle (LT^{-1})
$We = (dw^2\rho/\sigma)$	Weber number
μ	dynamic viscosity ($ML^{-1}T^{-1}$)
Φ	Harkins-Brown factor
$\Delta\rho = \rho_C - \rho_D $	difference of phase densities (ML^{-3})
ρ	density (ML^{-3})
τ	break-away time of drop (T)
σ	interfacial tension (MT^{-2})

Subscripts

C	continuous phase
D	dispersed phase
m	measured value
c	calculated value

REFERENCES

1. Grigar K.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1969.
2. Grigar K., Procházka J., Landau J.: *Chem. Eng. Sci.* 25, 1773 (1970).
3. Traube J.: *J. Prakt. Chem.* 34, 304, 515 (1886).
4. Lohnstein T.: *Ann. Phys.* 20, 237 (1906).
5. Harkins W. D., Brown F. E.: *J. Am. Chem. Soc.* 41, 499 (1919).
6. Hayworth C. B., Treybal R. E.: *Ind. Eng. Chem.* 42, 1174 (1950).
7. Ueyama K.: *Chem. Eng. Japan* 21, 755 (1957).
8. Null H. R., Johnson H. F.: *A.I.C.H.E.J.* 4, 273 (1958).
9. Null H. R.: *Thesis*. University of Tennessee, Knoxville 1955.
10. Rao E. V. L. N., Kumar R., Kuloor N. R.: *Chem. Eng. Sci.* 21, 867 (1966).
11. Siemes W.: *Chem. Ingr.-Tech.* 11, 727 (1956).
12. Siemes W.: *Dechema Monogr.* 29, 313 (1957).
13. Scheele G. F., Meister B. J.: *A.I.C.H.E.J.* 14, 9 (1968).

Translated by V. Staněk.