7. ———, and J. A. Tallmadge, *ibid.*, 744.
8. ———, Ph.D. thesis, Yale Univ., New Haven, Connecticut (August, 1964).
9. Jeffreys, H., *Proc. Camb. Phil. Soc.*, **26**, 204 (1930).
10. Levich, V. G., "Physicochemical Hydrodynamics," Chap. 12, Prentice Hall, Englewood Cliffs, New Jersey (1962).
11. Metzner, A. B., W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheol.*, **5**, 133 (1961).
12. Morey, F. C., *J. Research, U. S. Natl. Bur. Stands.*, **25**, 385 (1940).
13. Philippoff, W., in "Progress in International Research on Thermodynamic and Transport Properties," pp. 698-703, Academic Press, New York (1962).
14. Satterly, J., and G. Givens, *Trans. Roy Soc. Canada*, **27**, 145 (1933).
15. Van Rossum, J. J., *Appl. Sci. Res.*, **A7**, 121 (1958).
16. White, D. A., and J. A. Tallmadge, *Chem. Eng. Sci.*, **20**, 33 (1965).

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Coalescence of Liquid Droplets in Two-Component—Two-Phase Systems:

Part I. Effect of Physical Properties on the Rate of Coalescence

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Experimental coalescence time and time distribution studies of the coalescence of a single droplet at a plane interface are presented for four two-component–two-phase systems. The results have been analyzed by dimensional analysis and statistical analysis, and a correlation of coalescence time and coalescence time distribution with the physical properties of the system is proposed.

The coalescence of liquid dispersions is of great interest in many scientific fields, particularly in solvent extraction equipment where the generation of secondary mists result in entrainment and loss of efficiency. Therefore it is very important that the mechanism of the coalescence process is understood and that the effects of the physical properties of the participating phases on the rate of coalescence can be assessed.

Notable contributions to the understanding of coalescence mechanism have been made by Cockbain and Roberts (*1*), Elton and Picknett (*2*), Gillespie and Rideal (*3*), and many others. Also in recent years the studies by Charles and Mason (*4*) and Mackay and Mason (*5*) on the rate of thinning of the film between the droplet and the interface, and the work of Lang (*6*) on the effects of vibrations on this film, have resulted in proposals for the prediction of the rate of coalescence of single droplets at an interface in two-component–two-phase systems. The equations derived by these workers have been developed from the Navier-Stokes equation which specifies the physical properties of the phases and their significance in the systems to be studied. Furthermore the analysis was applied to drop-interface arrangements of specific geometry. Hence it would be very interesting to investigate the significance of all the possible physical properties of the system on the rate of coalescence, and the following paper presents the results of such a study. The investigation was initiated by a dimensional analysis of the problem, and the results of this analysis were further considered by a statistical analysis of a factorial experiment of the coalescence process. These aspects of the study are described, and a correlation relating coalescence time with the physical properties of the system is presented. This is followed in Part II with a description of high speed photographic work undertaken, and the flow characteristics of the film between the drop and interface are analyzed. This analysis has been applied to droplet-interface geometries obtained from the photographic studies in order to predict the pressure in the film at the mid point vertical axis and to compare it with the pressure inside the droplet in order to confirm the shape of droplets resting on an interface and explain the distribution of coalescence time results reported by all experimenters in this field.

EXPERIMENTAL APPARATUS

The all glass coalescence apparatus is shown in Figure 1 and was developed from that used in a previous investigation

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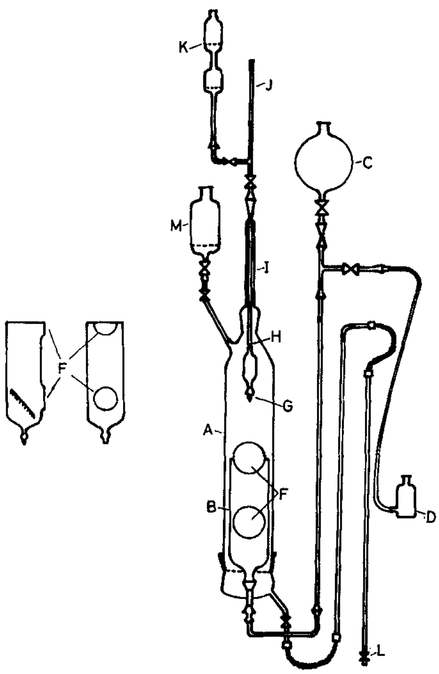

Fig. 1. Coalescence apparatus.

(7). It possessed an improved temperature control for both phases and permitted the interface to be easily cleaned and renewed. In addition provisions for adjusting the distance between the drop nozzle and the interface and for photographing drops were incorporated.

The cell consisted of a 50-cm. length of 7-cm. diameter Pyrex tubing *A* containing a short inner tube *B* which held the liquid-liquid interface at its open end. The interface was renewed by allowing liquid from the reservior *C* to overflow from the inner tube *B* into the annulus between *A* and *B*. The curvature of the interface was adjusted by raising or lowering the reservoir *D*. Circular plates *F* of optically flat glass were built into the tubes *A* and *B* to photograph the coalescence process.

The drop nozzle *G* was attached, by a small ground glass joint, to the tube *H* which made a sliding fit in the tube *I*, thereby making possible adjustment of the distance between the nozzle and the interface of approximately 1 to 12 cm. The expanded section, of 10-ml. volume, immediately before the nozzle provided sufficient residence time for the drop liquid to attain the same temperature as the surrounding continuous phase. Each drop nozzle consisted of a short length of precision bore capillary tubing sealed on to the socket part of a small ground glass joint. The end of each nozzle was carefully ground flat. Nozzles were constructed with diameters 0.3, 0.5, 1.0, 1.25, 1.5, and 1.8 mm.

The drop liquid was metered by a 5-ml. burette *J* equipped with greaseless taps. The drop liquid reservoir *K* was fitted with a sinter-disk filter plate.

The coalescence cell was mounted on a metal frame which could be raised from or lowered into the water bath measuring 12 in. square × 48 in. deep. The bath was constructed of galvanized steel with perspex windows in front, back, and sides. Water at a controlled temperature entered the bottom of the bath from a 20-gal. header tank and overflowed to a recycle tank, whence it was pumped back to the header tank. The header tank was equipped with a cooling coil and an immersion heater, and temperature control to ± 0.05°C. was achieved with a mercury-toluene regulator. The tanks and connecting lines were insulated, and the water bath was placed in a wooden air bath.

EXPERIMENTAL PROCEDURE

Each series of coalescence time determinations consisted of four operations: preparation of materials, cleaning the coalescence apparatus, assembling and filling the cell, and measuring coalescence times.

Materials Used

Analytical grade or redistilled reagents were used in all experiments. The phases were mutually saturated by prolonged mixing at the appropriate temperature.

Cleaning Procedure

All parts of the coalescence apparatus were degreased with acetone, rinsed with hot running tap water, and then immersed in a fresh solution of chromic acid. Following this the apparatus was thoroughly rinsed with fresh distilled water and finally dried in an oven. After it was cleaned, the apparatus was handled with great care, and during assembly none of the inner parts were in any way touched. The assembled cell was secured on the frame and lowered into the water bath, then filled with the two liquids to be studied. First the lower phase was introduced into the inner tube *B* from the reservoir *C*. A quantity was allowed to overflow into the annulus and the outlet syphon to the tap *L* made. The nozzle tip was lowered below the interface after which upper phase liquid was admitted from reservoir *M*. Following this the lower (drop) phase liquid was forced up the tube *I* to the burette by allowing more liquid to pass into the inner tube *B*. Finally the burette reservoir was filled and the nozzle raised to the required position. The cell and contents were allowed to come to thermal equilibrium with the water bath at the selected temperature before a series of coalescence time measurements were made.

Single drops or a series of drops could be formed by manipulating the burette tap, but single drops were difficult to form with the smaller nozzles. When a series of drops were studied, the rate of drop formation could be varied considerably. However it was necessary for the rate to be controlled so that the disturbance, caused by coalescence of one drop, subsided before the next drop reached the interface. In all experiments it was found that the assessment of fifty drops was sufficient to give a reproducible distribution of coalescence times for a given set of conditions.

The pump circulating cooling water was switched off when measurements were made, but periods with the pump off were restricted to about 30 min. In addition sufficient time was allowed after a change (temperature, nozzle size, etc.) to reestablish equilibrium conditions. This depended on the disturbance (physical or thermal) caused by the change. Finally the interface was flushed and renewed when necessary to remove possible contaminants.

Drop size was measured by observing the volume of liquid delivered by the burette for the formation of a known number of drops.

The liquids used were benzene, liquid paraffin, *n*-heptane, iso-octane, and water, Physical property data were obtained from the literature or measured by standard methods.

High and slow speed cine cameras were employed to photograph different aspects of the coalescence process.

RESULTS AND DISCUSSION

In all experiments it was found that step-by-step coalescence occurred; that is, a second smaller droplet was ejected from the larger drop during coalescence of the latter, and as many as seven such steps were observed in some experiments. Coalescence times were measured with a stopwatch and taken to be the interval between the arrival of the drop at the interface and its coalescence to form a secondary drop. This was termed *first step coalescence time*. In addition the time interval between the arrival of a droplet at the interface and its complete disappearance was measured. This was termed *overall coalescence time*. However it was difficult to obtain consistent and reproducible results, and many runs had to be rejected. It was found that accidental contamination of the liquids in the cell was the most likely cause of erroneous results, and therefore frequent checks on the drop size were made during each experiment. This indicated any change in interfacial tension resulting from contamination.

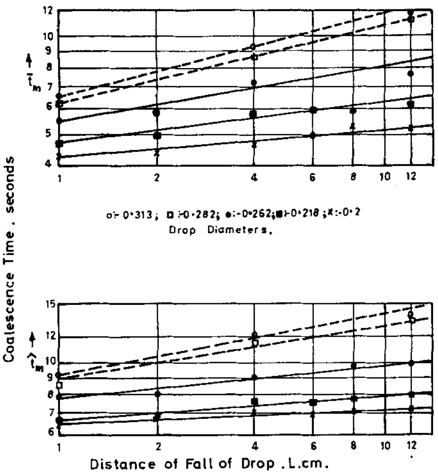

Fig. 2. Variation of coalescence time with distance of fall.

The mean coalescence time of the drops assessed in each experiment and the half life coalescence time (that is the time in which half of the drops assessed in each experiment coalesced) was calculated for first coalescence time and overall coalescence time. These have been given the symbols $\bar{t}_m$ and $\bar{t}_{1/2}$ for first step and $\hat{t}_m$ and $\hat{t}_{1/2}$ for overall coalescence times, respectively. It was observed that the mean coalescence time and the half life coalescence time were more reproducible than coalescence time distributions. There was little difference between $\bar{t}_m$ and $t_{1/2}$; the ratio $(\bar{t}_m/\bar{t}_{1/2})$ was 1.04 and the ratio $(\hat{t}_m/\hat{t}_{1/2})$ was 1.01 compared with the value of 1.1 reported by Charles and Mason (*4*).

A series of coalescence time determinations were made with the benzene-water system under various conditions to investigate the effect of changing the distance of fall (*L*) of the drop to the interface and to make a preliminary analysis of the variables affecting coalescence. It was observed that coalescence time increased with increase in the distance of fall, and this was confirmed in the other systems subsequently studied. Typical results for the benzene-water system for first step mean coalescence times $\bar{t}_m$ are shown in Figure 2; overall mean coalescence times $\hat{t}_m$ varied in a similar manner.

Variation of $\bar{t}_m$ with *L* was most likely the result of disturbances caused by impact of the drop with the interface. Such disturbances would increase as the energy possessed by the drop before impact increased, that is with increasing length of fall, drop size, and the approach velocity of the drop to the interface. It might be thought initially that an increased disturbance would reduce the drop stability, but the disturbance would eject the drop from the interface and thereby increase the thickness of the drainage film and consequently coalescence time.

The approach velocity of the drop to the interface after falling through heights of 1.0 to 12.0 cm. was estimated by cinephotography. The velocity increased to a constant value of 24 cm./sec. at about $L = 6.0$ cm. for water drops of radius 0.262 cm. falling through benzene at 25°C. Coalescence time measurements increased continuously with increase of *L*, and therefore the approach velocity alone cannot account for the variation in $\bar{t}_m$.

Lang (*6*) showed that amplitude of induced interfacial disturbances generated by a falling droplet at low velocity was

$$\alpha^2 = \frac{8\pi a^3}{3}\left(\frac{\rho_2 - \rho_1}{\rho_2 + \rho_1}\right)\frac{L}{A} \tag{1}$$

For a water drop of radius 0.262 cm. in benzene, the amplitude increases from 9% of the drop radius at $L = 1.0$ cm. to 30% of the drop radius for $L = 12.0$ cm. This is likely to have an increasing effect on the bouncing of the drop and therefore on the coalescence time as the distance of fall increases.

Previous workers disagree over the quantitative relation between coalescence time and drop size. Charles and Mason (*4*) report $\bar{t}_{1/2} \propto a^{3.15}$, whereas Lang (*6*) stated that $\bar{t}_{1/2}$ was independent of *a* for the system benzene-water. In this study it was found that $t_{1/2} \propto a$ for first step and overall coalescence times.

A dimensional analysis of the factors affecting coalescence time $\bar{t}_{1/2}$ with drop size *a*, continuous phase viscosity μ_2, difference in density between the phases $\Delta\rho$, and the interfacial tension γ was carried out and two dimensionless groups emerged:

$$\pi_1 = \left[\frac{\bar{t}_{1/2}\, a\, \Delta\rho\, g}{\mu_2}\right] \text{ and } \pi_2 = \left[\frac{\gamma}{a^2\, \Delta\rho\, g}\right]$$

π_1 was plotted against π_2 on logarithmic coordinates with first step coalescence time results for the system benzene-water. The slope of the line approximated to -1.0 suggesting that the group $[a\,\Delta\rho\, g]$ dominated the correlation, or that coalescence time is not affected by difference in density. Dimensional analysis is therefore inconclusive. However it is possible that the net effect of density difference would be small because the increased flattening of drop through increase of $\Delta\rho$ would cancel the increase in the drainage force.

It was therefore assumed the density difference did not affect coalescence time, and a factorial experiment was designed to study the significance of interfacial tension γ, continuous phase viscosity μ_2, drop size *a*, distance of fall of the droplet to the interface *L*, and temperature *T*.

These factors were studied at two levels with the systems in Table 1 used.

The level of each factor studied is reported in Table 2 which also gives the symbol of the factor used in the statistical analysis.

In Table 2, F_1, F_2, V_1, and V_2 are means for systems 1 and 2, 3 and 4, 1 and 4, and 2 and 3, respectively. A_1 and

TABLE 1. SYSTEMS STUDIED IN FACTORIAL EXPERIMENTS

System	25°C.		30°C.	
	μ_2	γ	μ_2	γ
1. Benzene and water	0.607	34.9	0.566	33.9
2. 50-50 benzene-liquid paraffin and water	2.22	41.0	2.01	40.1
3. 50-50 heptane-liquid paraffin and water	1.78	58.4	1.63	57.4
4. Iso-octane and water	0.507	55.3	0.477	53.8

TABLE 2. LEVEL OF EACH FACTOR IN STATISTICAL ANALYSIS

Factor	Symbol used in analysis	Level 1	Level 2	Units,
Interfacial tension	*F*	37.5	56.2	dynes/cm.
Viscosity	*V*	0.539	1.91	centipoise
Drop size	*A*	0.192	0.276	cm.
Descent distance	*L*	1.0	6.0	cm.
Temperature	*T*	25	30	°C.

Table 3. Values of $\overline{t_{1/2}}$ in Statistical Analysis

			A_1				A_2			
			T_1		T_2		T_1		T_2	
System			L_1	L_2	L_1	L_2	L_1	L_2	L_1	L_2
1.	V_1	F_1	4.05	4.85	3.69	4.35	6.0	7.50	5.80	7.20
4.		F_2	1.15	1.95	0.95	1.65	2.65	3.40	2.30	3.10
2.	V_2	F_1	7.63	8.98	6.32	7.94	11.86	11.69	8.34	9.52
3.		F_2	1.01	1.65	0.95	1.50	5.10	5.95	4.65	5.43

A_2 were the only levels of drop size for which $\overline{t_{1/2}}$ was determined for system 2.

The values of $\overline{t_{1/2}}$ employed in the statistical analysis are presented in Table 3. The times reported for systems 1.3 and 4 were interpolated from plots of $\overline{t_{1/2}} \cdot v \cdot a$ where necessary in order to obtain values of $\overline{t_{1/2}}$ corresponding to the levels A_1 and A_2.

Table 3 shows that $\overline{t_{1/2}}$ increases with increase of A, L, and V and decreases with increase of F and T. Comparison of the times for systems 3 and 4 at A_1 shows a decrease in $\overline{t_{1/2}}$ with increasing V instead of the expected increase. This suggests that possibly the times for system 3 at A_1 are too low.

The five-factor analysis was performed as described in Brownlee (*8*). It was split into two four-factor analyses for each level of V and T, respectively, and four three-factor analyses for each combination of F and V. Details of the statistical analysis are presented by Hawksley (*9*), and the following results were most significant.

1. All the variables affected $\overline{t_{1/2}}$.
2. The effect of drop size (A) depended on the level of interfacial tension (F) to an extent depending on the level of viscosity (V) and possibly temperature (T).
3. The effect of interfacial tension (F) depended on the level of viscosity (V) to an extent depending on the level of temperature (T).
4. The effect of descent distance (L) depended on the level of interfacial tension (F) to an extent depending on the level of viscosity (V).
5. The extent of temperature (T) depended on the level of viscosity (V).

The qualitative results of the statistical analysis were taken as the basis of the development of a correlation for $\overline{t_{1/2}}$ of the form

$$\overline{t_{1/2}} \propto [F^{x_1} \cdot V^{x_2} \cdot T^{x_3} \cdot A^{x_4} \cdot L^{x_5}] \qquad (2)$$

Conclusion (3) suggested that F and V effects were interdependent and both also depended on T. The effect of T was assumed to be the variation of F and V with temperature. The interaction of F with V was very small and was eliminated. Therefore the coalescence times reported in Table 3 were averaged over A, L, and T, and log $\overline{t_{1/2}}$ was plotted against log F and log V, respectively, in order to estimate the exponents x_1 and x_2. It was found that $x_1 = -2.$ and $x_2 = 0.5$.

Table 4. Effect of Phase Density Difference on K_1

System	K_1	$\Delta\rho$
1	4.26×10^4	0.1265
2	4.26×10^4	0.1230
3	8.37×10^4	0.233
4	13.5×10^4	0.311

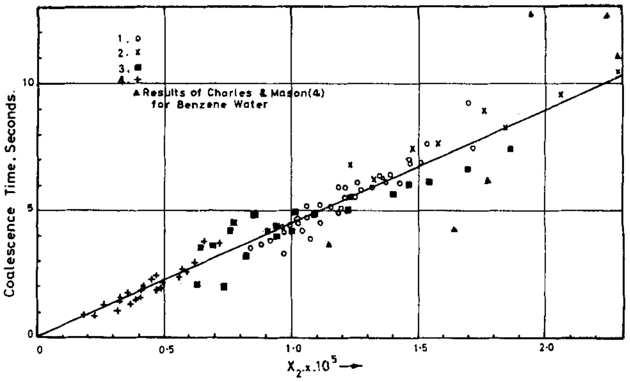

Fig. 3. Final correlation $t = K_2X_2$.

The exponent x_3 was thought to depend on V, and this was estimated by averaging $\overline{t_{1/2}}$ over F, A, and L; plotting log $\overline{t_{1/2}} \cdot v \cdot$ log $T/25$ to obtain values of x_3 at V_1 and V_2 and these were plotted as log $x_3 \cdot v \cdot$ log V. It was found that $x_3 = -0.7 \cdot V^{0.5}$. A similar procedure to that described for x_3 gave

$$x_4 = 0.02 \left(\frac{F^2}{V^{0.5}}\right)^{0.55} \text{ and } x_5 = 0.0001 \left(\frac{F^2}{V^{0.5}}\right)^{0.91}$$

Hence the proposed correlation is

$$\overline{t_{1/2}} = K_1 \left[\left(\frac{V^{0.5}}{F^2}\right)\left(\frac{T}{25}\right)^{x_3} (A)^{x_4} (L)^{x_5}\right] \qquad (3)$$

where x_3, x_4, and x_5 are as stated above.

A plot of $\overline{t_{1/2}}$ against the terms in the squared brackets of Equation (3) did not produce a single straight line suggesting that K_1 was dependent on some factor. K_1 appeared constant for systems 1 and 2 but progressively increased for systems 3 and 4 indicating that the phase density difference influenced K_1. The variation of K_1 with $\Delta\rho$ is shown in Table 4, where it can be seen that $\Delta\rho$ has a pronounced effect contrary to the indications of the dimensional analysis.

Further analysis showed that $K_1 = K_2 \, \Delta\rho^{1.2}$, and the final correlation in terms of the physical properties is

$$\overline{t_{1/2}} = K_2 \left[\left(\frac{\mu_2{}^{0.5}\, \Delta\rho^{1.2}}{\gamma^2}\right)\left(\frac{T}{25}\right)^{-0.7\mu_2{}^{0.5}} a^{0.02(\gamma^2/\mu_2{}^{0.5})^{0.55}} L^{0.001(\gamma^2/\mu_2{}^{0.5})}\right]^{0.91} \qquad (4)$$

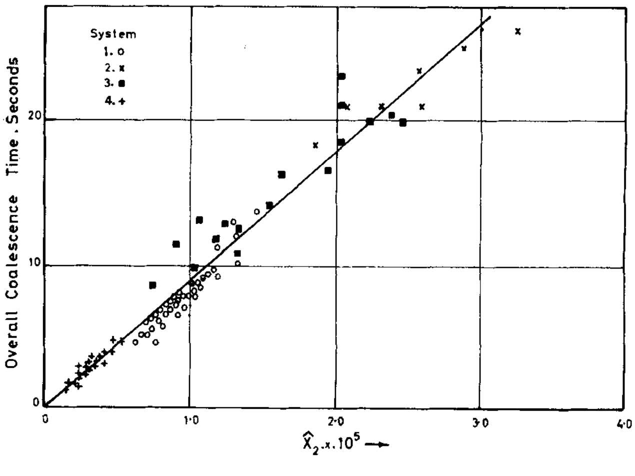

Fig. 4. Final correlation of overall coalescence times.

K was evaluated by plotting $\bar{t}_{1/2}$ against the terms in the square bracket of Equation (4) and computing K_2 by the method of averages (*10*). It was found that $K_2 = 4.53 \times 10^5$, and all the experimental results obtained in this investigation together with some published by Charles and Mason (*4*) are presented in Figure 3. From this figure it can be seen that the experimental results agree fairly well with Equation (4). The scatter is greatest for large coalescence times, but this would be expected because the distribution of coalescence times is very wide for large drops. Charles and Mason's results agree fairly well, but those of Konnecke (*11*) were found to deviate considerably. These were obtained from systems with low interfacial tension, and consequently the coalescence times were very short.

Prediction of the half life overall coalescence time $\hat{t}_{1/2}$ was attempted by studying the ratio $\psi = \hat{t}_{1/2}/\bar{t}_{1/2}$ in a similar manner to that described above. It was found that the most consistent trend was represented by

$$\psi = 1.96\, \mu_2^{0.5} \tag{5}$$

Multiplication of $\bar{t}_{1/2}$ obtained from Equation (4) by ψ gives $\hat{t}_{1/2}$. The overall coalescence time results are plotted in Figure 4 in terms of Equation (4) modified by Equation (5). There it can be seen that the scatter of the experimental results about the correlation curve is less than that given in Figure 3 for the first step coalescence time. Therefore the correction is considered to be satisfactory.

Finally several workers (*1, 3, 4, 7, 12*) have correlated experimental coalescence time distributions by the equation

$$\log \frac{N}{N_o} = -K(t - t_o)^{n_2} \tag{6}$$

while others have proposed (*2, 11*) an expression of the form

$$\log \frac{N}{N_o} = -ct^{n_1} \tag{7}$$

In addition Lang (*6*) has shown from theoretical considerations that the film between the drop and the interface must drain to a critical thickness before coalescence can occur. Hence the experimental first step coalescence time distribution results were compared with distribution times predicted by Equations (6) and (7) when it was found that there was little to choose between the two equations (9). Therefore Equation (7) was selected for correlation with the physical properties of the system. Values of n_1 were estimated for all the experimental first step coalescence time distributions by plotting log [log (N/N_o)] · v · t, and the mean value of n_1 for all results was 4.0 with a mean deviation of ± 1.1.

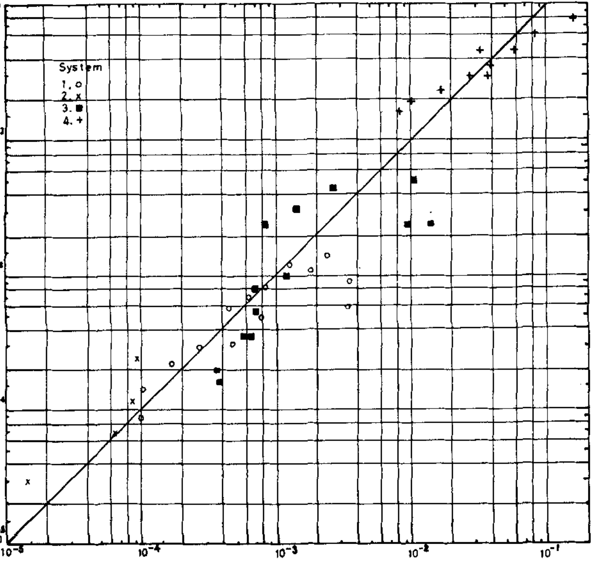

Fig. 5. Comparison of experimental and predicted values of constant c.

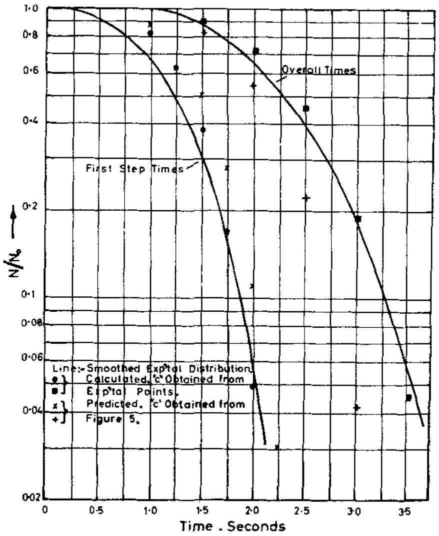

Fig. 6. Comparison of experimental, calculated, and predicted coalescence time distribution.

Since n_1 was found to be independent of the system studied, the coefficient c was correlated with physical properties through $\bar{t}_{1/2}$. Values of c were estimated for all systems studied by letting $t = \bar{t}_{1/2}$ and substituting $n_1 = 4.0$ and $(N/N_o) = 0.5$ into Equation (7) to give

$$c = 0.3\, (\bar{t}_{1/2})^{-4} \tag{8}$$

Therefore c can be predicted from the physical properties of the system since $\bar{t}_{1/2}$ can be predicted by Equation (4).

Values of c obtained from Equation (8) after calculating $\bar{t}_{1/2}$ by Equation (4) are compared in Figure 5 with the corresponding experimental values. The agreement between the predicted and experimental values of c is considered sufficiently good to permit an estimate of the first step coalescence time distribution to be made from the physical properties of the system. This is substantiated on Figure 6 in which the predicted values of (N/N_o) are plotted against t and compared with the values calculated from the experimental points and the smoothed experimental curves for the first step and overall coalescence time distributions. The same value of n_1 and c was used in the different distributions.

CONCLUSIONS

It may be concluded that a satisfactory correlation relating the first step half life and the overall mean half life coalescence time to the physical properties has been developed. The expression of the physical variables has been used to predict the coefficient in the coalescence time distribution equation which will enable a good estimate of the time required for a given percentage of drops of the same size and physical properties to coalesce.