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Rate of Coalescence of the Dispersed Phase in a Laboratory Mixer Settler Unit: Part I

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The rate of coalescence of large swarms of drops of a dispersed phase in the settler of a stage, laboratory mixer settler has been studied in order to establish the parameters that determine the dimensions of settlers used in extraction processes and effluent treatment. Part I is devoted to a description of the apparatus, experimental technique, and presentation of experimental results. Part II describes the development of a mathematical model which has been employed to analyze the results and is submitted as the basis for the design of settlers.

One of the most popular devices for contacting immiscible liquids in order to promote mass transfer is the mixer settler unit. This is due to its simplicity, ease of construction and operation, and the fact that high efficiencies can be expected irrespective of the characteristics of the liquids being treated. Thus, the mixer settler extractor may be considered in solvent extraction to be analogous to the bubble cap column in distillation. However, the performance of bubble cap distillation columns can be predicted fairly accurately, whereas techniques for the design or analysis of mixer settler extractors are nonexistent. Therefore, since these extractors are still being extensively employed in industrial applications, there is a need to establish criteria by which this equipment can be designed and analyzed.

A mixer settler extraction unit consists essentially of a number of stages, each of which contains a mixing chamber and a settling chamber. The mixer is usually provided with a propellor or turbine agitator and baffles, although in some, mixing is accomplished by means of a centrifugal pump. The emulsion generated in the mixer passes into the settling chamber through the mixed phase port and is distributed in the form of a wedge between the two phases in the settler. The dispersion wedge may exist above the interface if the more dense liquid is the dispersed phase, or below the interface if the less dense liquid is dispersed as illustrated in Figure 1. Settler operation is usually based on the principle that the emulsion wedge should not extend over the entire area of the interface, so that changes in throughput can be reflected in wedge length. If the wedge extends over the entire interface, increase in throughput must lead to an increase in the thickness of the wedge, with the result that raffinate tends to be lost through the extract port, and extract tends to pass through the raffinate port so that the efficiency of the unit is impaired. The problem of settler design is therefore an assessment of the factors that control the size of the emulsion wedge.

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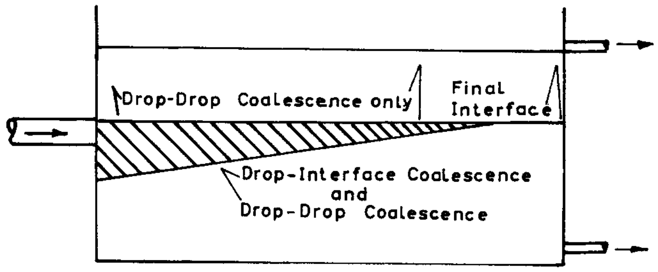

Fig. 1. Location of coalescence wedge when heavy phase dispersed.

The volume of the heterogeneous wedge between the phases is determined by the equilibrium between the rate of input of emulsion and the rate at which droplets of the dispersed phase coalesce at the surface of the emulsion. Drop-to-drop coalescence within the wedge does not reduce the volume of the wedge appreciably. Initially it was thought that the volume occupied by the emulsion could be determined from a knowledge of the flow rates of extract and raffinate in the settler, together with the results of static settling tests on emulsions formed in the mixer. However, Williams et al. (*1*) have shown that this is not possible and that emulsion settling rates are a function of both the surface area of the emulsion and the volume it occupies. It is evident that drop-to-drop coalescence occurs within the wedge, and droplets having a larger diameter than the mean exist at the emulsion surface. Coalescence of these droplets greatly affects the volume of the wedge and thus the capacity of the mixer settler extraction unit. Hence an investigation of the mechanism of coalescence in liquid-liquid dispersions should contribute to the establishment of procedures for the design of gravity settlers used in extraction processes. The following papers present the results of a study on a single stage, laboratory mixer settler. This part is devoted to the description of the apparatus and presentation of experimental results; Part II proposes a mathematical analysis of these results.

EXPERIMENTAL APPARATUS

The experimental investigation was carried out in a single stage mixer settler apparatus. The mixing chamber was a large

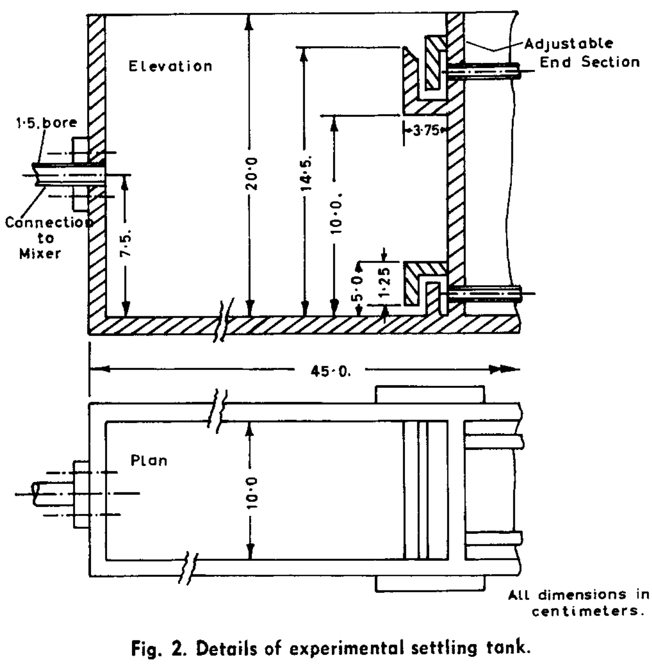

Fig. 2. Details of experimental settling tank.

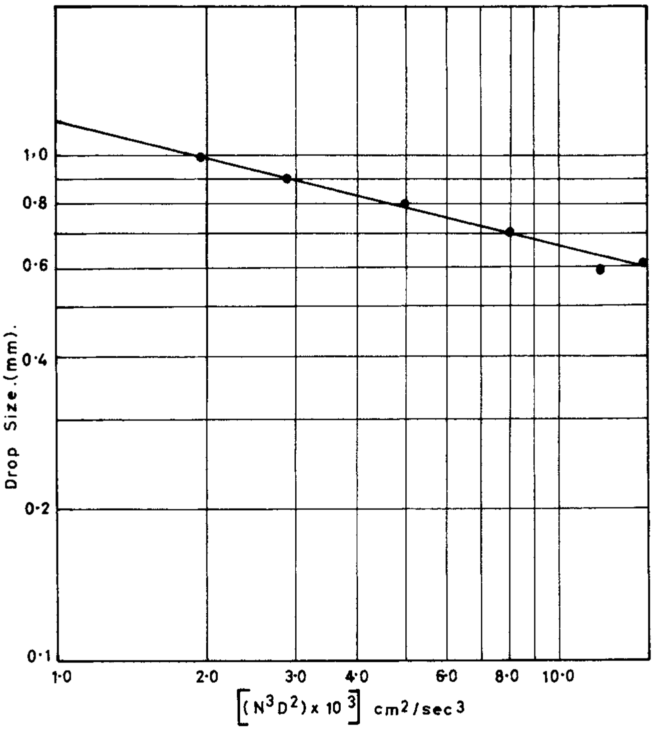

Fig. 3. Size of droplet entering settler.

beaker 26.2 cm. high and 12.8 cm. in diameter fitted with heavy and light phase inlet ports and a dispersed phase discharge port. The heavy and light phase inlet ports were constructed from 1.2 cm. bore glass tubing and arranged diametrically opposite each other at a height of 3.75 and 12.75 cm., respectively, above the base of the beaker. The exit for the emulsion was 1.5 cm. bore tube fitted at 90 deg. to the inlet ports, 8.25 cm. above the base of the beaker. Four removable baffles, each 1.25 cm. wide, were inserted vertically in the mixing vessel at positions 45 deg. to the inlet and outlet ports.

A four bladed brass paddle impeller 6.0 cm. diameter, 3.0 cm. wide attached to stainless steel shaft was used as agitator. The shaft passed through a brass bush bearing in order to eliminate whip and was driven by a 0.03 hp. electric motor. The speed of the agitator could be varied between 60 and 600 rev./min. by means of a speed reducing gearbox. The settler was constructed of perspex, and its dimensions are given in Figure 2. The end section containing the light and heavy phase discharge ports was secured to the remainder of the vessel by means of a brass clamping device which enabled the effective length of the settler to be adjusted to any length up to 45.0 cm. The disengaged phases leaving the settler were recirculated back into the mixing vessel, through 0.75-cm. O.D. copper tubing, by means of two centrifugal pumps. The pumps were fitted with bypass needle valves permitting fine control of the flow rate of each phase. Each pump was mounted on rubber pads to prevent vibrations being transmitted through the apparatus, and the flow rate of each phase was measured by a rotameter. The temperature of the circulating liquids was controlled at 25°C. by passing each phase through a copper coil immersed in a constant temperature water bath.

The experimental work was carried out to investigate the effects of initial drop size and volumetric throughput on the rate of coalescence of dispersions in settlers. However, occasionally, a secondary haze is formed in one or both phases during coalescence of some dispersions, and since these hazes would complicate the experiments, it was decided to use mixtures of kerosene and water in which the phase ratios were maintained at 2.1, as this system did not produce a secondary haze. Furthermore, coalescence rates for this system had been reported in the literature (*2*). The kerosene used in the experimental work was free from aromatics and therefore did not attack the perspex walls of the settler.

Table 1. Relation between Wedge Length and Drop Input Rate

Wedge length, cm.	Agitator speed, rev./min.	Initial drop size, mm.	$\frac{Q}{d_0^3} \times 10^{-4}$	Mean value of $\frac{Q}{d_0^3} \times 10^{-4}$
5	250	0.9	2.06	
	300	0.8	2.05	
	350	0.7	2.05	
	400	0.6	2.05	2.055
10	250	0.9	4.06	
	300	0.8	4.08	4.065
	350	0.7	4.08	
	400	0.6	0.04	
15	250	0.9	6.12	
	300	0.8	6.12	6.135
	350	0.7	6.18	
	400	0.6	6.12	
20	250	0.9	8.22	
	300	0.8	8.20	8.23
	350	0.7	8.25	
25	250	0.9	10.40	
	300	0.8	10.50	10.47
	350	0.7	10.48	
	400	0.6	10.50	
30	250	0.9	12.30	
	300	0.8	12.40	12.39
	350	0.7	12.45	
	400	0.6	12.40	

EXPERIMENTAL PROCEDURE

The apparatus was thoroughly cleaned and assembled, and the pipework and pumps were primed with the approriate liquid. The stopcock in the transfer line between the mixer and settler was closed, and the required volumes of distilled water and kerosene were placed in the settler. Following this, the mixer was charged with the requisite amount of the two liquids, and the agitator was started at a speed selected for the particular experiment. After 15 min. agitation, the stopcock in the transfer line was opened and the phases were circulated at the chosen rate for 3 hr. at 25°C. in order to ensure that the phases were mutually saturated. After this, samples were taken from each phase in the settler and the density, viscosity, and interfacial tension determined. The results obtained were compared with the initial physical data and, if satisfactory, the experiment was continued and the heterogeneous wedge was photographed in the manner described below.

At the conclusion of the experiment, the pumps and the stirrer were switched off, and the static settling time of the dispersion in the mixer was noted in order to obtain some indication of the amount of surface active contaminant present. These were generally found to be in good agreement with the initial static settling time, provided that there was no contamination and the physical properties remained constant.

Before any photographs were taken, the interface was cleaned by removing a portion of each phase from the surface. The flow rate for the particular experiment was then maintained constant for at least 30 min. before a photograph was taken. Following this, photographs were taken at 10 to 15 cm. increments along the upper and lower surface of the emulsion with the aid of two mirrors set at 45 deg. above and below the wedge. In addition, a photograph of the side elevation of the wedge was also taken, and the diameters of the droplets at different wedge lengths were determined from the photographs. All photographs were taken at 32f aperture setting and a shutter speed of 1/25 sec. Back lighting, by means of an electronic synchronized flash, was used as recommended by Kintner (3).

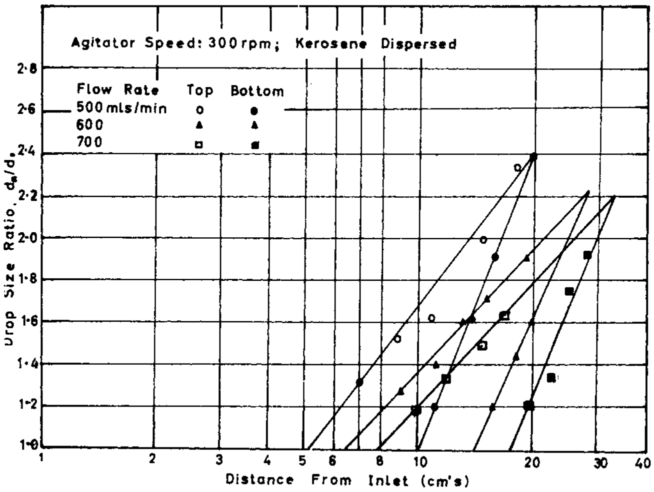

Fig. 5. Variation of drop size with distance from inlet.

EXPERIMENTAL RESULTS

The size of the droplets entering the settler were estimated in the initial experimental work. Agitator speeds were chosen to produce a uniform emulsion, but care was taken to ensure that no air was entrained into the liquids. Photographs showed that the size of the droplets entering the settler was fairly uniform, and a plot of [ln d_0] v [ln N^3D^2] is shown in Figure 3. From this figure it appears that the size of the droplets forming the coalescence wedge is a function of $N^{-0.75}$ and $D^{-0.5}$, suggesting that the initial drop size in the wedge can be estimated from an equation of the form

$$d_0 = C \cdot N^{-0.75} \cdot D^{-0.5} \cdot \rho^{-0.375} \cdot A(h_0)^{0.375} \quad (1)$$

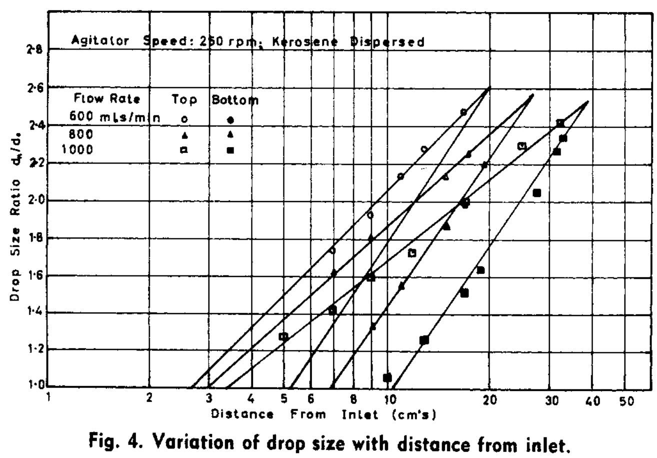

Fig. 4. Variation of drop size with distance from inlet.

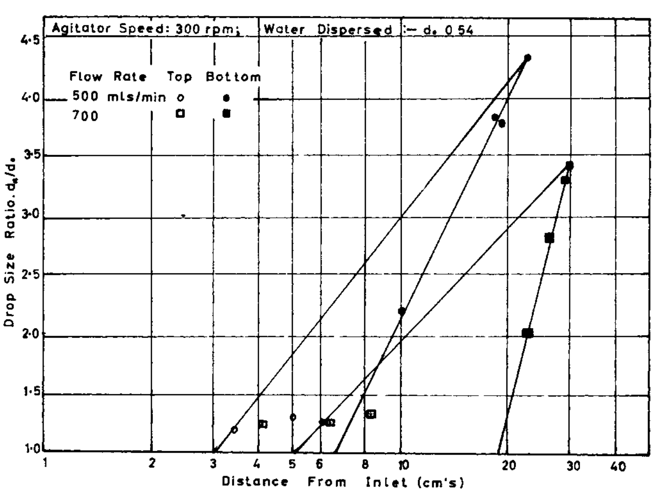

Fig. 6. Variation of drop size with distance from inlet.

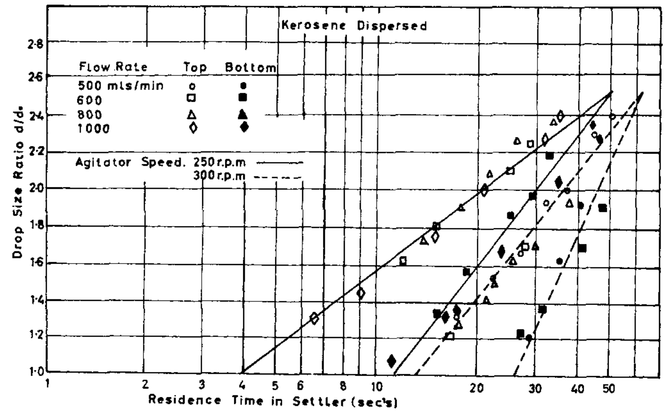

Fig. 7. Effect of residence time on drop size.

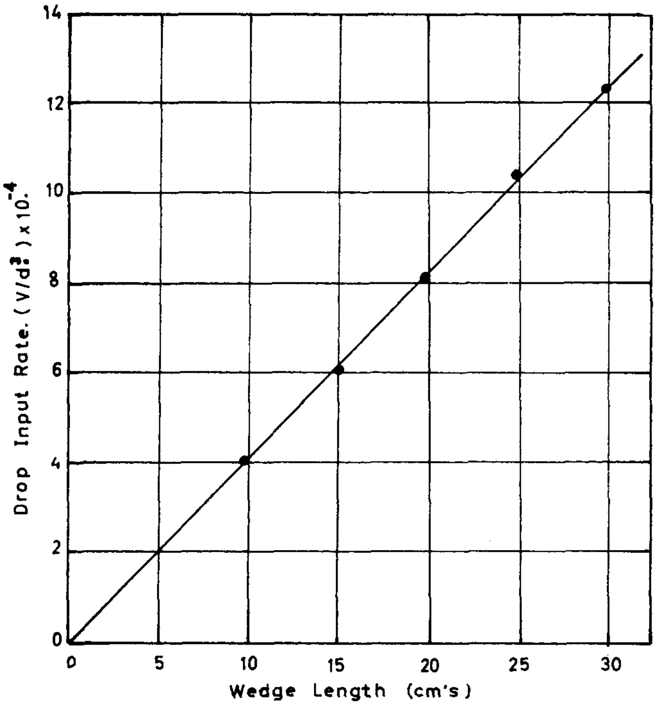

Fig. 8. Effect of drop input rate on wedge length.

similar to that proposed by Shinnar and Church (*4*) for the prediction of drop size in agitated emulsions.

Experimental results were obtained from dispersions of kerosene in water with a phase ratio of 2:1 kerosene to water and from dispersions of water in kerosene with a phase ratio of 2:1 water to kerosene. The droplet sizes for the upper and lower emulsion surfaces in the settler were measured at the different distances from the inlet for varying volumetric throughputs and agitator speeds. The measured droplet sizes were tabulated by subdivision into groups of size range 0.3 mm. for agitator speeds of 250 rev./min. and 0.2 mm. for a speed of 300 rev./min. From the frequency of these groups, mean diameters were calculated from the relation

$$d_{AV} = \frac{\Sigma nd}{\Sigma n} \quad (2)$$

Finally, in order to obtain a comparison between the effects of various impeller speeds, the increase in the mean drop size was determined from the relation $\alpha = (d_n)/(d_0)$ and plotted against distance from the inlet of the settler. Typical results are shown in Figures 4, 5, and 6.

DISCUSSION OF RESULTS

The relationship between drop size, position in the settler, and the dispersed phase flow rate is shown for dispersions of kerosene in water in Figures 4 and 5 and for dispersions of water in kerosene in Figure 6. These results are converted into plots of increase in drop size vs. residence time in the settler in Figure 7.

All experimental results confirm that there is a region in the vicinity of the emulsion inlet in which turbulence and other entry effects are damped out and the drops pack close together to form a fairly stable configuration. This section extends a short distance along the length of the settler, and within this length there appears to be no coalescence. Thus, Figure 7 shows that for drops of size 0.9 mm. entering the settler, it takes 4 sec. before any increase in size is noticed at the top of the wedge and 10 sec. on the lower surface. Thereafter the increase in the size of drops is greatest at the top surface where both drop-to-drop and drop-to-interface coalescence occur simultaneously. At the lower surface where only drop-to-drop coalescence occurs, the increase in drop size is delayed until the wedge has thinned considerably. This picture corresponds with the observations made by Rodgers. Trice, and Rushton (*5*) during static settling tests. This would be expected, since the continuous phase must drain through the interstices between the drops from the top of the wedge to the bottom, thereby impeding coalescence in the lower layers of the wedge.

It is interesting to note that when the experimental results presented in Figures 4, 5, and 6 expressed in terms of wedge length are converted into increase in drop size vs. residence time in the settler, the different curves corresponding to different dispersed phase flow rates coincide to give a single plot depending only on the initial drop size as shown in Figure 7. A different curve was obtained for each entry drop size which suggests that the capacity of a settler depends on the size of the drops entering the settler and their residence time. Furthermore, the drainage of the continuous phase from the space in between the drops will depend on the number of drops present in the wedge, and therefore the droplet input rate was plotted against wedge length as shown in Figure 8. It can be seen that all the results fall onto a straight line, indicating that the length of a coalescence wedge in a gravity settler is proportional to the droplet input rate. The data used in constructing Figure 8 is shown in Table 1.

In conclusion it may be stated that the experimental results presented above and their analyses enable a picture of the coalescence processes taking place in a settler to be formulated. This gives a basis for the development of a mathematical model which is presented in Part II of this work. There the results are further analyzed, and proposals are made for the design of gravity settlers.

NOTATION

$A(h_0)$ = energy required to separate two droplets of unit radius from an initial distance h_0 to infinity
C = constant in Equation (1)
D = diameter of agitator
d = diameter of droplet
d_0 = initial diameter of droplet
l = wedge length
N = revolutions per minute
n = number of droplets
Q = dispersed phase flow rate
α = ratio of drop sizes d/d_0
ρ = density

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Part II. The Analysis of Coalescence in a Continuous Mixer Settler System by a Differential Model

Part II of this paper deals with the analysis of continuous separation of an unstable emulsion in a gravity settler of a mixer settler unit. When the emulsion passes from the mixing vessel into the settler, droplets of the dispersed phase approach one another to form a heterogeneous zone between the two liquid phases. The formation of this zone is determined by the local velocity gradients and the density difference between the phases. In the mixing zone, a high level of turbulence is generated to optimize mass transfer between two liquid phases, but in the settler all turbulence must be rapidly damped out, and the velocities of the phases in the settling tank must be low and controlled only by the throughput rates. The position of the heterogeneous layer with respect to the final interface between the settled phases will be determined by the density of the dispersed phase, and the liquid droplets in this layer tend to attain some stable packing arrangement determined by the diameter of the drops. It is important in any settling tank to prevent extract phase from being entrained with raffinate leaving the settler and vice versa. This difficulty can be overcome by suitable design and positioning of off-take lines and by operating the unit in such a way that the heterogeneous layer does not occupy the total available cross-sectional area between the phases in the settler. Under such conditions, the size of the heterogeneous wedge formed is determined by the throughput rates and by the physical properties affecting coalescence of the droplets, such as interfacial tension and viscosity of the liquids.

MODEL

Consider the behavior of the wedge of drops in more detail. Let the dispersed phase consist of drops of the more dense liquid; then the wedge is formed above the interface. At the lower surface of the wedge, droplets are coalescing with the bulk liquid phase by a drop-interface coalescence mechanism. Inside the wedge and at the upper surface, drops are coalescing together by a drop-drop coalescence mechanism. The residence time or life of the droplets in the wedge is controlled by these two processes.

Consider a settler of unit width operating under steady state conditions with the dispersed phase made up of the more dense liquid when a wedge of droplets will be formed above the interface, as shown in Figure 1. Consider a small increment δl in the wedge at a distance l from the inlet. Let the depth of the wedge at this position be h, let the number of drops entering the element per second be n, and let the mean diameter of the drops be ϕ. In practice, a distribution of drop sizes will exist at any position in the wedge. If uniform sized droplets enter the wedge, variation in sizes is brought about by variations in coalescence times. This will be discussed later in more detail. However, in this analysis a mean drop diameter will be considered. The volume of dispersed phase entering per second is equal to the volume of dispersed phase leaving the element, plus the volume of dispersed phase coalesced with the lower interface per second. Coalescence between droplets in the element will not affect the material balance. This mechanism of coalescence will result in an increase of the mean drop diameter in the element from ϕ to $\left(\phi + \frac{d\phi}{dl}\right)$. Thus, the material balance for the dispersed phase gives

$$\frac{n\pi\phi^3}{6} = \left(n - \frac{dn}{dl}\,\delta l\right)\frac{\pi}{6}\left(\phi + \frac{d\phi}{dl}\,\delta l\right)^3 + \frac{\pi\phi^3}{6}\left(\frac{1}{\tau^*}\,\frac{\delta l\,\eta^*}{\pi\phi^{2/4}}\right) \qquad (1)$$

The droplets have been considered as rigid spheres, and in the range of drop sizes studied in this work, 0.08 to 0.30 cm., this assumption is valid. Expanding Equation (1) and considering first-order terms only, we get

$$\frac{3}{\phi}\,\frac{d\phi}{dl} - \frac{1}{n}\,\frac{dn}{dl} + \frac{4}{\pi}\,\frac{\eta^*}{\tau^*}\,\frac{1}{n\phi^2} = 0 \qquad (2)$$

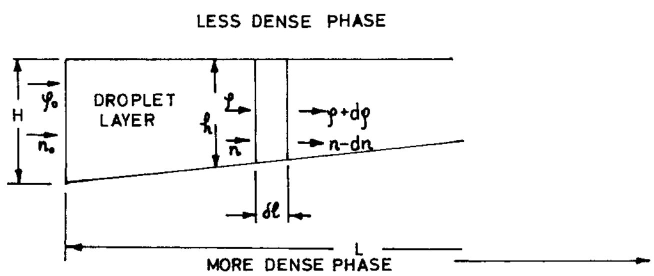

Fig. 1. Parameters of the differential model.

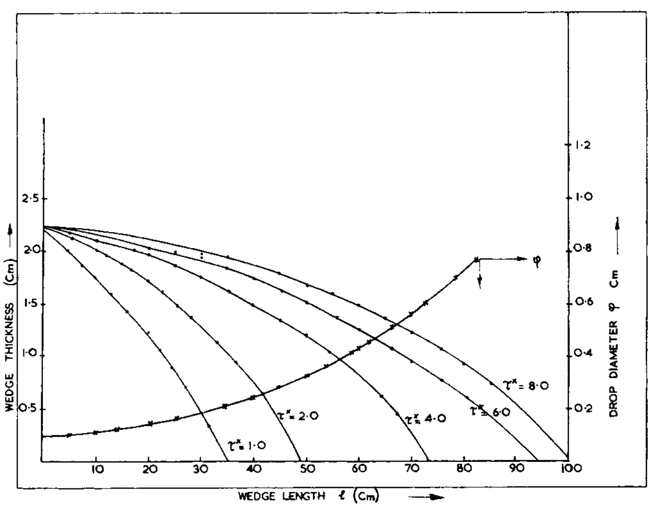

Fig. 2. Wedge thickness and drop diameter vs. wedge length. τ = 4.0 sec.