Hydrodynamic Characterization of Mixer-Settlers in Extraction of Zirconium with TBP

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ABSCTRACT: *An experimental study has been made of the hydrodynamics of a stage mixer-settler to obtain appropriate design information. In this paper several tests were done according to full factorial design of experiments with high reliability, since each test recurs seven times and the results of them are very close to each other(P=1bar and T=25 °C). Sauter diameter in each test is determined with photographing of both mixer and settler and holdup quantity is measured by vacuum pump at the end of each test. In each test, dispersion height and dispersion length are determined by photographing of settler. Sauter diameter has been compared with Calderbank model and finally, a model has been suggested*

KEY WORDS: *Mixer-Settler, Dispersion height, Dispersion length, Drop size, Dispersed phase hold up, Tri-butyle phosphate.*

INTRODUCTION

A counter-current multistage extraction column having high performance (i.e., high extraction efficiency and large maximum throughput) has been developed. The hydrodynamic behavior and the mass transfer characteristics of the column have been analyzed experimentally.

The Wide variety of equipment now available for liquid-liquid extraction includes mixer-settlers, centrifugal extractors, and spray, packed, pulsed, and rotary agitated columns. However, the simple box-type mixer-settler, incorporating up to 16 separate stages, is still widely used for handling high flow ratios.

One reason is that mixer-settlers can be operated at high efficiencies, more or less regardless of the properties of the phases. Scale-up on a semi empirical basis is often possible, although it does not always result in an optimum design. For any particular design of mixer-settler, the limits on volumetric throughput and energy input are governed by the system properties; for example, low interfacial tension systems tend to result in smaller drops with poor settling characteristics. [1]

Surprisingly, the simple mixer-settler itself has not been thoroughly investigated. Typically, a specific process, or what is claimed to be a novel design, has been

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operated to obtain data on “Overall” efficiency and volumetric capacity specific to the extractor and extraction process studied. However, numerous studies have been made of mass transfer efficiency in agitated tanks. Studies have also been made of the hydrodynamics of vertical or horizontal gravity settlers in the absence of mass transfer, both with and without coalescing aids. These studies provide a fundamental understanding of the basic processes involved-such as interfacial phenomena and drop-drop interactions, but the experimental conditions are usually quite unlike those in continuous liquid-liquid mixer-settlers [2-4].

Although the settler is generally the volumetric capacity limiting item in a mixer-settler train, little information is available upon which to base an optimum design; design is largely empirical or stems from pilot plant experience. The methods commonly employed are based either on the residence time of the phases or the thickness of the dispersion (or wedge) in the settler. New settler designs have, however, been developed and applied industrially by *Mizrahi* and *barnea* (I.M.I) (1973) and *Stoner* and *Wohler* (Lorgi) (1975) for specific metallurgical processes.

However, important design parameters have been ignored, for example, the geometry of the settler as related to the mixer design, coalescence characteristics inside the settler, and phase stability to ensure minimum entrainment. Industrial settlers are usually operated in a mode whereby the wedge extends across the entire length of the settler, thereby enhancing the probability of mutual phase entrainment. Industrial equipment seldom operates under steady-state conditions. Process fluctuations typically occur, and this often results in severe phase entrainment. Further, the mixers are usually over designed through lake of data relating to volumetric capacity. Evaluation of a design procedure for a mixer-settler unit requires knowledge of the system hydrodynamics. At present, no consistent hydrodynamic data is available on continuous operation. Most of the current work tends not to deal with system hydro-dynamics [5,6].

A detailed experimental study has been therefore carried out on the hydrodynamics of a continuous mixer-settler in a pilot-scale multistage cascade to obtain design criteria. The work included investigation of (a) dispersion characteristics in the mixer: drop-size distribution, mean drop size and dispersion phase hold up (b) settler characteristics: wedge length, height and separation mechanism of phases. In this context, phase inversion refers to the interchange of phases in an agitated two-phase system such that the dispersed phase becomes continuous and vice versa under conditions determined by system properties, phase ratio, and energy input. *Sarkar et al.* (1980) pointed out the importance of phase inversion in defining the limiting volumetric capacity of agitated columns, and some analogous effects have been observed in the present study.

Although a 10-stage cascade has been operated, the hydrodynamic data presented have been obtained from a single stage since no significant change was found in the hydrodynamics from stage to stage [7,8].

Table 1: Physical properties of system at P=1bar and t=25 ºC.

Physical Properties	Tri-butyle phosphate(TBP) 60 %, Kerosene insteed organic phase and HNO3(3.5 M), Zirconium OxyCloride(12 g/lit)
μd (cp)	2.58
μc (cp)	0.958
ρd (gr/cm^3)	0.907
ρc (gr/cm^3)	1.204
γ(dyne/cm)	32.16
Dc (m^2/s)	4.251×10^{-8}
Dd (m^2/s)	4.60×10^{-8}

EXPERIMENTAL

Materials

Chemical systems which are used in this set contain Tri-Butyle Phosphate(TBP) 60 %, Kerosene instead of organic phase and HNO3(3.5 M), zirconium oxycloride (12 g/lit) instead of aquase phase. Organic phase is dispersed and zirconium is solute, so it transfers between two phases. Physical properties of system are given in table 1.

Methods

Experiments are designed according to full factorial way and submitted in table 2. Several tests have been done with high reliability, since each test recurs seven times and the results of them are very close to each other. Sauter diameter in each test is determined by photo-graphing both mixer and settler and holdup quantity is measured by vacuum pump at the end of each test,

Table 2: Effective factors in experimental section at P=1 bar and t=25 ºC.

1-Volume fraction of TBP to Kerosene in organic phase	One case: Volume fraction of TBP to kerosene is 60 %	
2- Concentration of nitric acid	One case: 3.5 Molar	
3- Concentration of Zirconium Oxy Chloride	One case:12 g/lit	
4-Flow rate of Organic phase to Aquase phase(Vd/Vc=k, Vd,Vc: mlit/min)	Three case:	
	1.k>1	
	2.k<1	
	3.1. K=1 ; Only in drop sizing	
	3.2. k>>1; Only in dispersion parameters	
5-Impeller speed(rpm)	Four case:	
	750	
	800	
	900	
	1 000	

Table 3: Parameters of Mixer-Settler.

Parameters	Definition
Constructed	glassware
Number of stage	10
Dimension of system (cm)	150×125×100
Capacity of mixer(milt)	100
Diameter of mixing vessel(mm)	37
Capacity of settler(milt)	250
Settler diameter(mm)	50
Length of settler(mm)	125
Length of vessel after baffle(settler)(mm)	20
Length of separation vessel(mm)	45
Mixer diameter(mm)	24
Mixer gum(mm)	15
Speed(rpm)	1-1 000
Flow rate of pump(pulls/min)	0-120

so the ratio of organic phase quantity to quantity of both organic and aquase phases is hold up.

Settler characteristics were studied by photographing a wedge by means of mirrors inclined at 45º above and below the settler. This procedure enabled the upper and lower surfaces of the wedge to be viewed and photographed. Wedge dimensions were measured and photographed over a range of phase flow rates and energy input to the mixer. Baffles positions of 125 mm and 145 mm from the phase input were used.

Devices

The continuous countercurrent mixer-settler was incorporated (Fig. 1). Mixing vessel is provided with a turbine and settler is provided with two vertical baffles. Phase separation occurred in horizontal cylindrical settlers constructed of industrial glassware. The ratio of the mixed volume to the available settler volume was approximately 1:2.5. The ratio of impeller to vessel diameter (D/DT) was taken as 0.34, consistent with standard tank configurations [9]. Parameters of the device are given in table 3.

Two vertical disk baffles were installed opposite the inlet to each settler. The "ideal" liquid-liquid, mutually saturated, system TBP 60 %, Kerosene-HNO_3, 3.5 M was used in the investigation. In most runs, HNO_3 was the continuous phase. Direct photography was used for drop-size measurement.

At the start of each run the mixers and settlers were filled with two liquids until the height of liquid in the mixer was equal to the mixer diameter and the interface was at the mid-position in the settler. After the agitator speed was set, feed and solvent flow rates were adjusted to give the required ratio of Vc: Vd.

THEORY

Drop Size

Initially, the Sauter mean droplet diameter was determined as a function of time in order to determine the time for dispersion equilibrium. In all cases, 10 min. was found to be sufficient for achievement of equilibrium, resulting in a homogeneous dispersion with a relatively small drop size distribution. The critical speed for substantially uniform dispersion was approximately 700 rpm for system. The Sauter mean drop diameter was calculated from the usual expression as Equation (1).

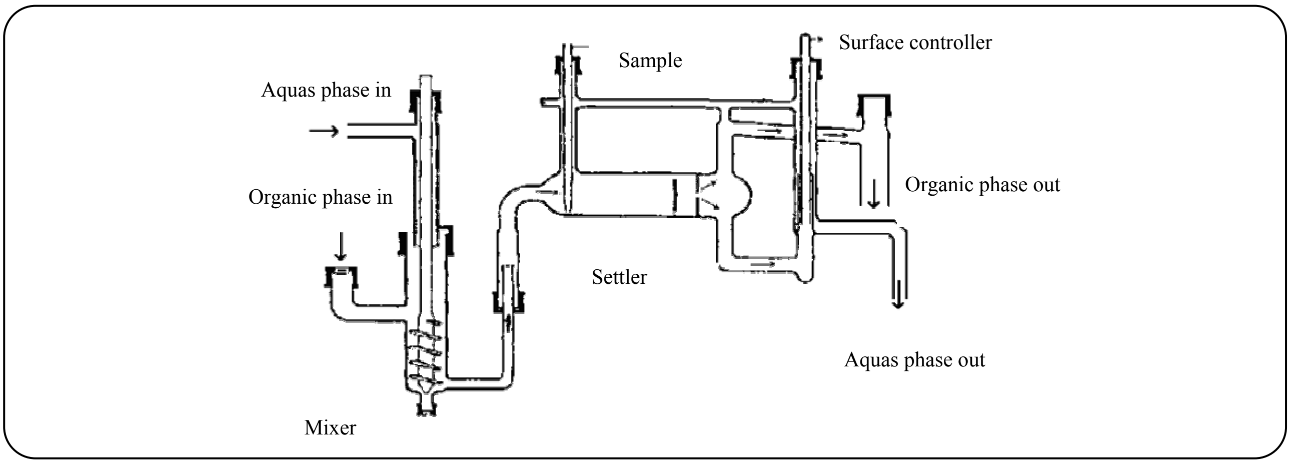

Fig. 1: Flow diagram of a stage of extraction system in a mixer settler unit.

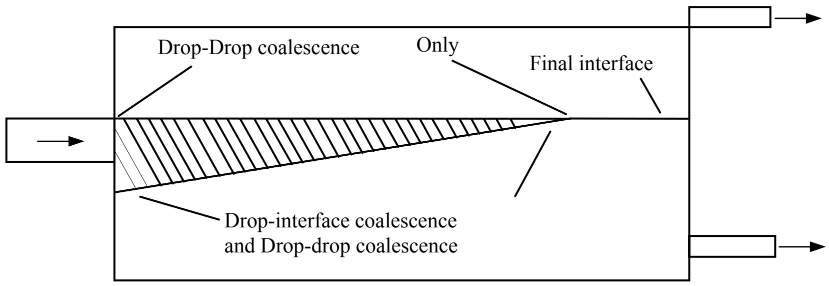

Fig. 2: Dispersion wedge when organic phase is distributed.

Table 4: Experimental results of experience (Sauter diameter and Dispersed phase hold up).

N (rpm)	Vd (milt/min)	Vc (mlit/min)	Hold up	Qd/Qc	d32 (mm)
750	59	45	0.50	1.31	0.26
800	59	45	0.48	1.31	0.23
900	59	45	0.46	1.31	0.20
1 000	59	45	0.40	1.31	0.17
750	50	50	0.42	1.00	0.19
800	50	50	0.41	1.00	0.18
900	50	50	0.40	1.00	0.17
1 000	50	50	0.38	1.00	0.15
750	42	53	0.36	0.79	0.15
800	42	53	0.32	0.79	0.14
900	42	53	0.28	0.79	0.13
1 000	42	53	0.26	0.79	0.12

$$d_{32} = \frac{\sum nd^3}{\sum nd^2} \tag{1}$$

Results of experiences about drop size are presented in table 4. There are two types of Liquid - liquid extraction:

a) Primary dispersion: in this dispersion drop size is more than 100 micron.

b) Secondary dispersion: in this dispersion drop size is less than 1 micron.

Dispersion Wedge in settler

Component of dispersion wedge in horizontal settler is illustrated in Fig. 2. The upper line of wedge is coalescence band and the bottom line is settling band, and after necessitous time two phases separate.

Settler characteristics were studied by photographing a wedge by means of mirrors inclined at 45º above and below the settler. This procedure enabled the upper and lower surfaces of the wedge to be viewed and photographed. Wedge dimensions were measured and photographed over a range of phase flow rates and energy input to the mixer. Baffles positions of 125 mm and 145 mm from the phase input were used [10,11].

RESULTS AND DISCUSSION

Drop distribution

It is studied about primary dispersion in this paper as shown in table 4. Dispersed phase hold up is specified as method and results of these experiences are shown in table 4 and illustrated in Fig. 3. In this, variation of Sauter diameter (d32) versus hold up in constant impeller speed is delineated. Another proposition that is studied, and has economic and industrial significance is drop size distribution in different conditions such as different impeller speeds and different ratios of organic phase flow rate to aquase phase flow rate, so optimum condition for extraction in experience system has occurred.

Drop size distribution curves are illustrated in Figs. 4 and 5. In these curves, ratio of number of droplets that have contiguous average Sauter diameter in a group to total population of droplets (d ×n / d_n) versus amount of Sauter diameter of this group, is charted.

The range of drop sizes observed in the mixer was mainly between 0.12 and 0.26 mm, characteristic of those normally found in agitated aqueous organic systems. In all cases some droplets were produced in the secondary dispersion size range of less than 0.1 mm, but these will create no difficulty in the settler because, at the used energy inputs, they were a small proportion of the dispersed phase. Drop size distributions were measured in a range of rotor speeds and phase flow rates. Figs. 4 and 5 are typical of the distribution curves obtained. The Sauter mean drop diameters were found to be distributed, consistent with the observations of *Giles et al.* (1971), but contrary to those of *Rodger et al*. (1956). However, precise comparison is difficult since drop sizes are very much dependent on the geometrical configuration of the contactor [10].

A mode proffer

Experimental values of d32 were compared with the correlation of Calderbank (1958) that is shown in Equation (2):

$$\frac{d_{32}}{D} = 0.06(1+3.75\phi)(We)^{-0.6} \quad (2)$$

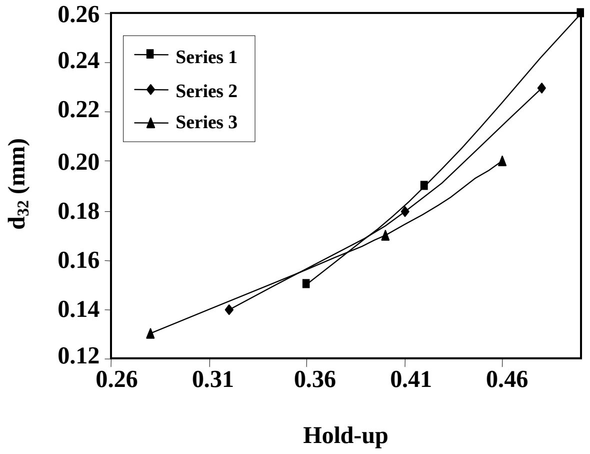

Fig. 3: Sauter mean drop diameter vs. holdup with different constant impeller speeds.

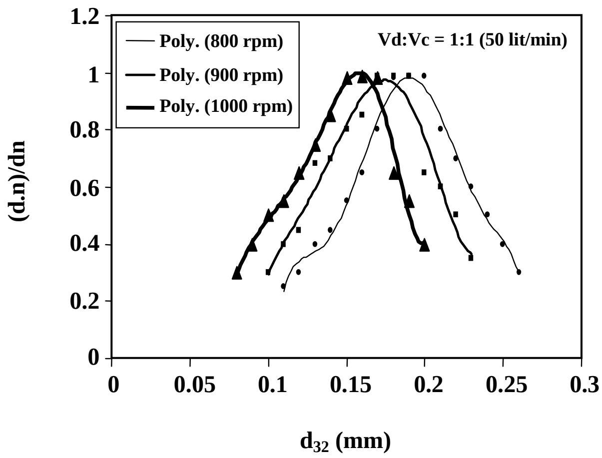

Fig. 4: Drop size distribution with impeller speed.

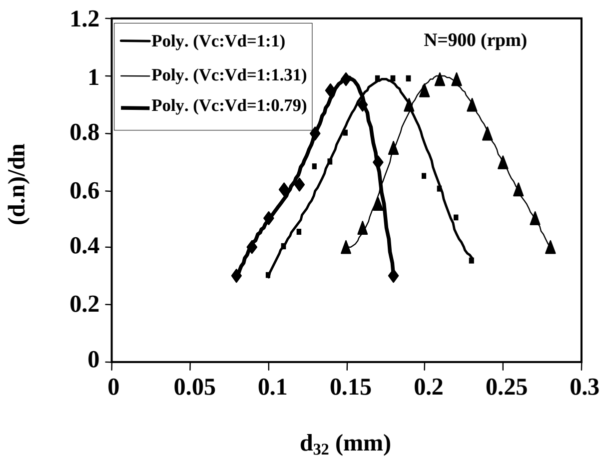

Fig. 5: Drop size distribution with volume fraction of droplets.

The difference is probably due to the different geometric configurations of the mixing systems, and also to the presence of a settler in the present work, which creates a back pressure related to the wedge dimension; that is, the greater the hindrance, the larger the back pressure. Under steady state conditions, momentum transfer in the mixer-settler interconnection enhances the level of turbulence in the mixer.

No correlation has previously been published for drop size and holdup in the mixer of a continuous mixer-settler. Such a correlation can be derived by dimensional analysis of the physical properties of the system, operating conditions, and the impeller geometry as submitted in Equation (3).

It is assumed that Webber number is dimensionless and D, N and σ are agitator diameter, impeller speed and surface tension respectively. It is observed that d32 depends on dispersed phase hold up directly as shown in table 4, so a relationship for experience Sauter diameter versus dimensionless parameters as dispersed phase hold up and Webber number is proposed in Equation (5). [11,12]

$$d_{32}=f(N,V_d,V_c,\mu_d,\mu_c,\sigma_i,\rho_m,D) \quad (3)$$

$$We=\frac{D^3N^2d_{32}}{\sigma_i} \quad (4)$$

$$\frac{d_{32}}{D}=a(1+b\phi)(We)^c \quad (5)$$

Calculation of the exponents of the experimental results yields table 5 and is presented in Equation (6) as Suggested model:

$$\frac{d_{32}}{D}=0.508(1+23.70\phi)(We)^{-0.6} \quad (6)$$

It describes the data with a correlation coefficient of 0.92. Fig. 6 shows that the measured experimental value lies within $\pm$ 7 % of those calculated by using Equation (6).

We compare both Suggested model and Calderbank model in tables 6 and 7; the result of comparison is that error of Suggested model is much more than Calderbank model in this system. Error in tables 6 and 7 is calculated by sum of lest square method. And eroor of calderbank model is 10.91 % and Suggested model is 10 %.

Table 5: Parameters of Equation (5).

a	b	c
0.508	23.70	-0.6

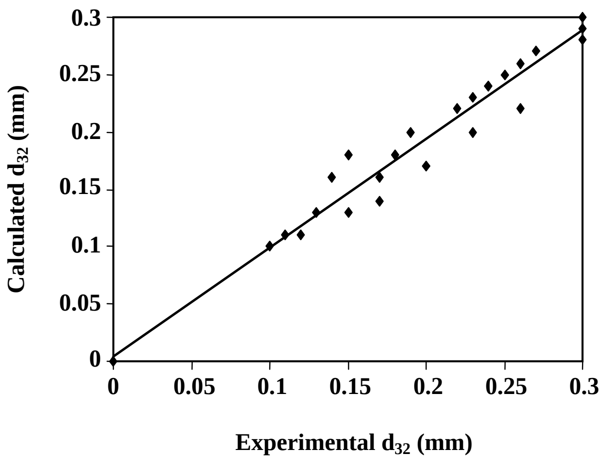

Fig. 6: Evaluation of experimental data with this model.

Dispersion Height and Dispersion Length

Results of experiences about wedge of dispersion are presented in table 8. Drop sizes in the wedge in the settler were found to be in the range 0.12 to 0.26 mm. Unlike in the mixer, no satellite secondary drops were detected in the settler although some must have been carried over with the continuous phase. Normally the baffle was continuous phase wetted, but as part of the investigation, the optimum sized baffle was also made preferentially wetted in the disperse phase by suitable surface treatment. The length and height of the wedge were measured over a range of phase ratios, energy input, and baffle sizes for dispersions of both the organic and the aqueous phase. The effects of these parameters on wedge characteristics are illustrated in Figs. 7 and 8 [12-14].

In these Figures height and length of dispersion versus dispersed phase hold up in different constant impeller speeds are compared, and variation of dispersion wedge versus Sauter diameter in different constant impeller speeds is studied. It is observed that dispersion wedge revolves directly in constant impeller speed versus holdup, and it is changed versus Sauter diameter in constant impeller speed vice versa.

CONCLUSIONS

- The mean drop size varies with the rotor speed, dispersed phase holdup, and system physical properties,

Table 6: Terms of Suggested model at laboratory conditions, P=1 bar and T=25 ºC.

N(rpm)	Vd(milt/min)	Vc(milt/min)	Hold up	Experiment (d32)	Suggested model	Error
750	42	53	0.36	0.15 000	0.18 552	0.00 126
800	42	53	0.32	0.14 000	0.15 462	0.00 021
900	42	53	0.28	0.13 000	0.11 942	0.00 011
1 000	42	53	0.26	0.12 000	0.09 870	0.00 045
750	59	45	0.5	0.26 000	0.25 010	0.00 010
800	59	45	0.48	0.23 000	0.22 293	0.00 005
900	59	45	0.46	0.20 000	0.18 613	0.00 019
1 000	59	45	0.4	0.17 000	0.14 443	0.00 065
750	50	50	0.42	0.19 000	0.21 320	0.00 054
800	50	50	0.41	0.18 000	0.19 304	0.00 017
900	50	50	0.4	0.17 000	0.16 389	0.00 004
1 000	50	50	0.38	0.15 000	0.13 789	0.00 015
					sum of least square error	0.00 393

Table 7: Terms of Calderbank model witch all tests are done at laboratory conditions.

N(rpm)	Vd(milt/min)	Vc(milt/min)	Hold up	Experience d32	Calderbank	Error
750	42	53	0.36	0.15 000	0.18 352	0.00 112
800	42	53	0.32	0.14 000	0.15 901	0.00 036
900	42	53	0.28	0.13 000	0.12 864	0.00 000
1 000	42	53	0.26	0.12 000	0.10 921	0.00 012
750	59	45	0.5	0.26 000	0.22 452	0.00 126
800	59	45	0.48	0.23 000	0.20 237	0.00 076
900	59	45	0.46	0.20 000	0.17 099	0.00 084
1 000	59	45	0.4	0.17 000	0.13 824	0.00 101
750	50	50	0.42	0.19 000	0.20 110	0.00 012
800	50	50	0.41	0.18 000	0.18 340	0.00 001
900	50	50	0.4	0.17 000	0.15 687	0.00 017
1 000	50	50	0.38	0.15 000	0.13 409	0.00 025
					sum of least square error	0.00 604

Table 8: Results of dispersion and hold up experiences.

N(rpm)	Vd(mlit/min)	Vc(mlit/min)	Vd/Vc	Dispersed phase hold up	Dispersion height(mm)	Dispersion length(mm)
750	42	53	0.79	0.36	32.70	120.00
800	42	53	0.79	0.32	35.06	141.92
900	42	53	0.79	0.28	39.24	146.00
1 000	42	53	0.79	0.26	39.39	146.18
750	59	45	1.31	0.50	31.16	120.00
800	59	45	1.31	0.48	33.95	122.00
900	59	45	1.31	0.46	37.06	147.11
1 000	59	45	1.31	0.40	37.23	148.11
750	65	25	2.60	0.64	41.44	149.74
800	65	25	2.60	0.61	44.36	154.65
900	65	25	2.60	0.59	45.08	156.22
1 000	65	25	2.60	0.56	47.49	158.11

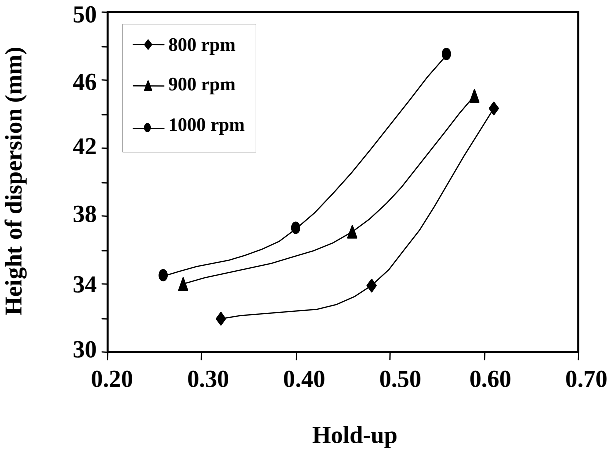

Fig. 7: Height of dispersion vs. Hold-up.

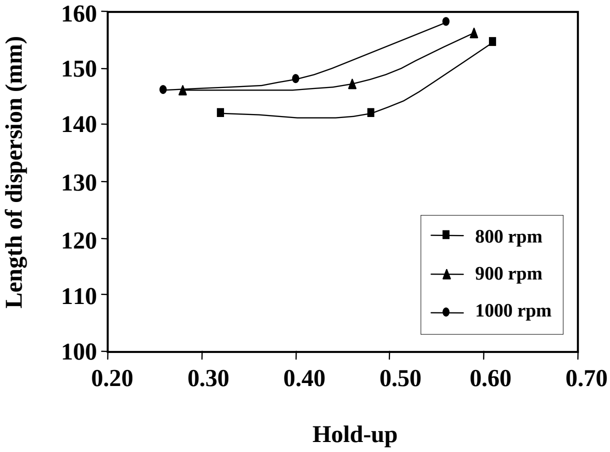

Fig. 8: Length of dispersion vs. Hold-up.

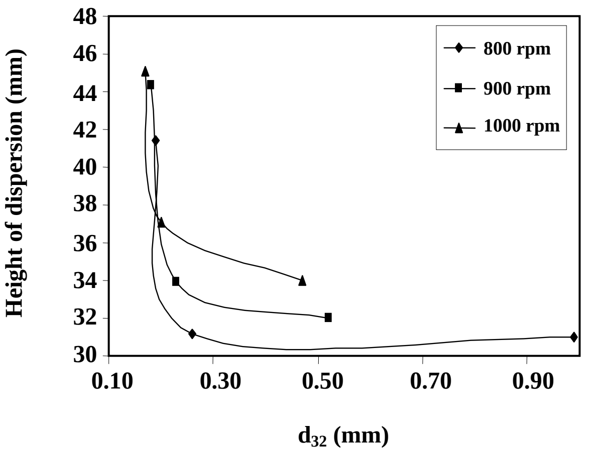

Fig. 9: Height of dispersion vs. hold-up at different impeller speed.

as illustrated in Fig. 2. At low rotor speeds the variation in drop size is greater than the higher speeds. This results due to a drop residence time distribution in the mixer, and only a proportion of the drops spent a sufficient time in the discharge region of the impeller to cause breakup. No attempt was made to measure any variation in drop size with position in the vessel since, provided the critical speed was exceeded, conditions in the relatively small vessel were homogeneous, as confirmed by the absence of any holdup profile. Fig. 2 illustrates that the Sauter mean drop diameter at constant rotor speed increases with holdup due to coalescence effects. As holdup increases the probability of droplet collision followed by subsequent coalescence also increases.

- For experimental system, both dispersion height and length increase with increasing dispersed phase flow rate, increasing continuous phase flow rate and increasing agitator speed as illustrated in Figs. 7, 8 and 9. All of these parameters affect drop size and dispersed phase hold-up in the mixer and hence coalescence and flow in the settler.

- When the dispersed phase throughput was increased at fixed agitator speed and continuous phase flow rate, both height and length of dispersion increased as illustrated in Figs. 7 and 8. The increase in height and length corresponding to an increase in the flow of the continuous phase was only about one-third of that produced by the same increase in the flow rate of the dispersed phase.

- In general, an increase in throughput causes the axial velocity component of the drops to be much higher than the vertical component, thus hindering drop-interface coalescence, and resulting in an increase in wedge length.

- When the rotor speeds were varied at a fixed dispersed phase throughput, the wedge length increased by approximately 10 % for every 100 rpm increment. At high energy input levels, that is, at about 1000 rpm the small drops (0.1-0.25 mm diameter) produced required a long time to coalescence.

- It is observed after interring of dispersion in the settler, its shape is similar to wedge, and after about one hundred seconds, it is separated. With constant impeller speed, height of dispersion increases directly against volume fraction, and both coalition and separation bands decrease versus volume fraction, and interface height decrease too. In constant volume fraction of phases, dispersion height increases directly versus impeller speed, and both coalition and separation bands decrease versus impeller speed, and interface height decrease too.

Nomenclature

D	Mixing vessel diameter (mm)
d	Drop diameter (mm)
dn	Average diameter of a group
d_{32}	Sauter mean drop diameter (mm)
N	Rotor speed (Rpm)
n	Number of drops
Vd, Vc	Volumetric flow rate of the dispersed and continuous phase, respectively (milt/min)
We	Webber number, ($We=D^3N^2d_{32} / \sigma_i$)
a, b, c	Exponents in Equation (2)
μ	Viscosity (centipoises)
ρc	Continuous phase density (g/cm^3)
σ	Interfacial tension (Dyne/cm)
ϕ	Dispersion phase hold up
H	Height of dispersion (mm)
hc	Coalition band (mm)
hs	Separation band (mm)

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