

A SIMULATION MODEL FOR TWO- AND THREE-PHASE AGITATED SYSTEMS

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Abstract—A simulation model was developed to analyze the hydrodynamics of dispersions in agitated batch and continuous systems. The model enables the drop size distribution and average drop size to be calculated from given physical and operating properties of the system. Agreement between calculated and experimental results for two-phase liquid–liquid systems is satisfactory. The extension of the model to three-phase, liquid–liquid–solid, systems enables the hydrodynamics of crystallization in dispersions to be described, while accounting for the kinetics of nucleation and crystal growth. Size distributions and average sizes of the free drops, the crystals and the conglomerates (mother liquor containing crystals) can be simultaneously calculated. However, due to the limited data available, comparison was restricted to the experimental system of aqueous Na_2SO_4 dispersed in kerosene. Additional correlations relating the functional dependence to the various parameters in three-phase systems are required before a general predictive model for three-phase systems can be realized.

INTRODUCTION

Numerous studies (Hinze 1955; Vermeulen 1955; Sprow 1967a; Chen & Middleman 1967; Mlynek & Resnick 1972; Shiloh 1970; etc.) have been devoted to the study of drop size distribution and average drop size in dispersed systems. Most efforts were aimed at determining the functional relationship between the physical properties, operating conditions, and drop size distribution in agitated two-phase, liquid–liquid, systems.

Hillestad & Rushton (1966) presented a 'simulation' model whereby equisized drops containing a reactant coalesced with identical drops containing another reactant, and separated immediately to their original sizes. The reaction rate was studied, assuming complete mixing in the coalescence stage. The coalescence probability of all the drops was assumed to be identical. Shah & Ramkrishna (1973) utilized the integro-differential massbalance technique to calculate the time dependent reaction rate in a dispersed phase which contained one reactant while the other reactant was in the continuous phase. Spielman & Levenspiel (1965) utilized the Monte Carlo technique to analyse two-phase dispersion flow through a pipe. The model enabled the drop distribution along the pipe to be calculated. Shiloh (1970) utilized the Monte Carlo technique to extend Hillestad and Rushton's approach to a drop population of a nonuniform size which is affected by the hydrodynamics of the system. However, only a small localized population could be analysed to yield the local size distribution. Zeitlin (1970) and Zeitlin & Tavlarides (1972) extended Spielman and Levenspiel's approach to a mixing vessel. Nonuniform drops were treated in a grid representing a vertical cross-section through the center of the vessel. The motion of the drops was controlled by the hydrodynamics of the system. However, the grid mesh size was, by necessity, too large for a true representation of the system.

Shiloh *et al.* (1971, 1972, 1973, 1975) studied a three-phase system in which crystallization occurs in a saturated aqueous phase while being dispersed in an organic continuous phase. The 'drops', consisting of mother liquor and crystals, are denoted as conglomerates. The inert continuous phase liquid enables to maintain a constant temperature for the crystallization process. As shown by Shiloh *et al.* operation with this three-phase crystallization system allows good control over the nucleation and crystal growth rate. Crystals which are 1.8 times larger than those produced in equivalent two-phase crystallizers can be obtained. Obviously, the performance depends on the rate of coalescence of the conglomerates with the feed stock, i.e. the feed droplets of the mother liquid which are continuously introduced into the system (while the conglomerates and the solids within them are continuously extracted from the system).

This study is aimed at developing a simulation model which will describe the hydrodynamics

of two and three-phase systems, and form the basis for the study of the kinetics of the three-phase crystallization system. The model, based on the Monte Carlo technique, was constructed in two stages.

First, a model for analysing the hydrodynamics of a two-phase mixing system was developed to determine the average drop size and drop size distribution from the given physical properties of the system and the operating parameters.

Second, the two-phase model was extended to account for the presence of the solid crystals in the dispersed phase and to calculate the size distribution and average diameter of the conglomerates, the crystals and the free drops in the system.

THE SIMULATION MODEL FOR THE TWO-PHASE SYSTEM

The two-phase system is contained in a cylindrical mixing vessel equipped with baffles. The two-phases are immiscible and the dispersed phase occupies but a small fraction of the total volume of the fluid in the system. As mixing proceeds, the motion of the impeller imparts momentum to the two-phases and the dispersed drops may collide, coalesce and/or break. Under steady state conditions the break-up and coalescence rates are balanced and the drop-size distribution (and average drop size) in the system is practically constant. The construction of a useful simulation model requires the stipulation of a number of assumptions and simplifications:

1. Angular symmetry is assumed. This enables the system to be described as a plane cutting the container across its center, thus yielding a planar two-dimensional system.

2. Assuming a mirror symmetry defines the borders of the system as the vertical wall of the vessel and the axis of the impeller, the fluid interface and the bottom of the container (figure 1).

3. Following Zeitlin (1970, 1972) the vessel is divided into two operating regions: a mixing region and a coalescence region. Their relative proportions are determined by the velocity field (see assumption 13 below).

4. In the planar two-dimensional presentation, a drop is represented by a circle.

5. Two neighboring drops which have at least one point of contact define a collision event.

6. The drops in the system may be stable until they reach a certain maximum size. The maximum drop diameter d_{\max} is given by the following correlation:

$$d_{\max} = K \cdot \left(\frac{\sigma}{\rho_c} \right)^{0.6} \frac{\phi^c}{N^{1.2} \cdot D^{0.8}} \quad [1]$$

where K represents a characteristic constant of the system; σ represents the interfacial surface tension between the two fluids; ρ_c denotes the density of the continuous phase; ϕ represents the dispersed phase hold-up; N represents the r.p.m.; D the diameter of the agitator and $c = 0.21$ for $\phi < 0.008$, $c = 0.29$ for $0.008 < \phi < 0.07$, $c = 0.3$ for $0.07 < \phi < 0.15$, $c = 0.37$ for $0.15 < \phi < 0.27$.

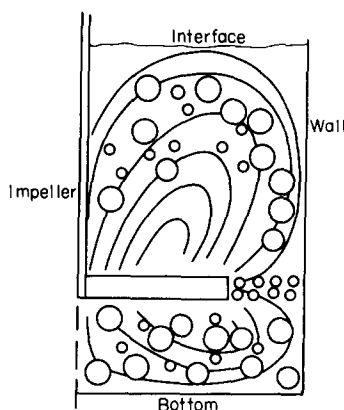


Figure 1. Vertical cut along the center of the system.

The values of c were derived from the experimental data of Brown & Pitt (1972). Essentially similar correlations are given by Hinze (1955) and Vermeulen *et al.* (1955).

7. Following Levich (1962), we assume that a minimum drop size exists in the system. This minimum drop size is mainly produced in the mixing region and is given by the following correlation

$$d_{\min} = \left(\frac{\nu_c^3 \rho_c}{E} \right)^{1/4} = 33.74 \times 10^8 \nu_c^{3/4} N^{-3/4} D^{-5/2} (\text{m}) \quad [2]$$

where E is a specific power input into system, and ν is the kinematic viscosity.

8. The mixing region is characterized by drop break-up. Every break-up is binary, forming a pair of random-sized but complementary drops. Each drop can be divided into 2^n droplets. It is assumed here that $n_{\max} = 2$, i.e. large drops will only break twice. Smaller drops may only break once, or not at all. Since drops smaller than d_{\min} cannot be formed, any 'break-up' which leads to values smaller than d_{\min} is 'cancelled'.

9. The coalescence region is characterized by coalescence as well as break-up of the drops.

10. If a drop which is formed by coalescence is larger than the stable maximum drop size in the system, it will immediately break into two complimentary random parts, each smaller than the stable maximal size.

11. The probability for break up of drops smaller than the maximum stable drop size is proportional to the square of the drop size (related to the maximum stable drop size in the system), i.e. to d^2/d_{\max}^2 (Zeitlin 1970).

12. The coalescence rate between drops is given by the correlation of Hillestad & Rushton (1966):

$$R_i = 3.77 \times 10^{-10} \cdot N^{0.73} \cdot D^{0.81} \cdot T^{-0.2} \cdot \phi \cdot \mu_c^{-0.98} \cdot \mu_d^{0.024} \cdot \rho_c^{4.23} \cdot \sigma^{4.74}, \quad [3]$$

$$R_d = 33.54 \times 10^{16} \cdot N^{-3.5} \cdot D^{-7.7} \cdot T^{5.05} \cdot \phi^{1.58} \cdot \mu_c^{-0.26} \cdot \mu_d^{-1.3} \quad [4]$$

where the coalescence rate R is expressed as (100×) the ratio of the dispersed phase volume which coalesces in a second to the total volume of the dispersed phase; N is given r.p.m.; T is the diameter of the dispersed phase; D is given in r.p.m.; T is the diameter of the vessel, (in ft) and μ_c and μ_d denote the viscosity of the continuous and dispersed phase, respectively.

Equation [3] applies when coalescence rate increases with the mixing rate, while [4] applies when the coalescence rate decreases with the r.p.m. The criteria for choosing either [3] or [4] is given by the critical Weber number, as given by Hillestad & Rushton (1966):

$$We_{\text{crit}} = 0.343 \cdot 10^{0.075(T/50)^2} Re^{0.75} \quad [5]$$

where $We \equiv D^3 N^2 \rho_c / \sigma$ and $Re \equiv D^2 N \rho_c / \mu_c$. Thus, [3] is used when the calculated Weber number of the system is smaller than the critical Weber number. Equation [4] is used when the critical Weber number is smaller than the Weber number of the system. Obviously both equations apply when $We_{\text{system}} = We_{\text{crit}}$.

13. The motion of the drops in the system is determined by two vectors: (a) The continuous phase velocity vector u , which is defined by the following type equations proposed by Zeitlin (1970):

$$u_z = K_1 f_1 \left(\frac{z}{H}, \frac{r}{T} \right) f_2(N, D, T, H), \quad [6]$$

$$u_r = K_2 g_1 \left(\frac{z}{H}, \frac{r}{T} \right) g_2(N, D, T, H) \quad [7]$$

where z and r are the vertical and radial coordinates and H is the height of the fluid in the vessel.

(b) The velocity vector \mathbf{V} describing the settling or buoyancy of a drop, as given by Love (1965):

$$|\mathbf{V}| = \frac{29.05 \cdot |\rho_c - \rho_d|^{0.58} \cdot (d)^{0.7}}{\rho_c^{0.45} \cdot \mu_c^{0.11}} \quad (\text{m/sec}) \quad [8]$$

The local velocity of a drop is calculated by combining the above vectors and its motion is therefore defined according to its position in the vessel.

EXTENSION TO THE THREE-PHASE SYSTEM

The simulation model for the two-phase system has been extended to account for the crystallization process in the three-phase system. For lack of functional relationships between the various parameters, the following additional data and stipulations were used. These relate to the particular system of a saturated aqueous Na_2SO_4 solution which crystallizes while dispersed in kerosene, as experienced by Shiloh (1970):

1. The diameter of the conglomerate in the system is one order of magnitude larger than that of the crystal free drops. Hence, it is assumed that the maximum stable conglomerate linear size is 10 times larger than the maximum stable drop size in the system.
2. The rate of coalescence between the conglomerates is 16 times larger than that between the free drops in the system.
3. The rate of coalescence between drops and conglomerate is 3 times larger than that of the free drops coalescing between themselves.
4. Crystal growth rate is constant and relates to the linear growth of the crystal.
5. The nucleation rate is constant at a given temperature and volume of the system.
6. The conglomerates' motion may be described as the motion of drops by utilizing [6]–[8] and by neglecting the slip velocity between the conglomerates and continuous phase.

The calculation procedure

The general flow chart for the simulation model is presented in figure 2, and only the special features of the model which affect the calculation procedure will be elaborated here.

Machine limitations and computation time restrict the Monte Carlo technique to a limited 'sample size', or number of 'drops', participating in the stochastic process considered here. Clearly, the number of drops chosen represents a compromise between the computation time and expected accuracy. Some 450 drops were found to represent the best compromise, and increasing this number to 2000 drops yields an insignificant (0.5%) change of the results.

Shiloh (1970) related the finite number of drops samples in the model to a local region in the vessel. Zeitlin (1970) related his sampled drops to the whole vessel and 'operated' on wide arbitrary grid. Here, the sampled drops are 'placed' in the grid so as to maintain the true dispersed phase hold-up of the system, and the distance between the drops in the model corresponds to the real system. This implies that the dimensions of the vessel must be 'scaled down' so that the given dispersed phase will fill the matrix which fits the 'scaled down' boundaries of the vessel. In practical terms this procedure means that the chosen sample of drops is divided between the mixing and coalescence regions in proportion to their relative areas in the plane of operation.

The coalescence rates are given by [3] or [4] (modified for the three-phase system by the above-mentioned additional data), and a 'cycle' is arbitrarily defined as a given number of coalescences. The stochastic process is thus allowed to proceed until this cycle is completed, i.e. the number of calculated coalescences in the model reaches that predicted by utilizing the above equations. To assure steady state, the cycles are repeated until the size distribution is practically constant. For the continuous system the given flow rates are maintained by introducing (or extracting) particles to or from the system at the end of each cycle. Also, if applicable, new nucleates are introduced and allowance is made for crystal growth before starting a new cycle.

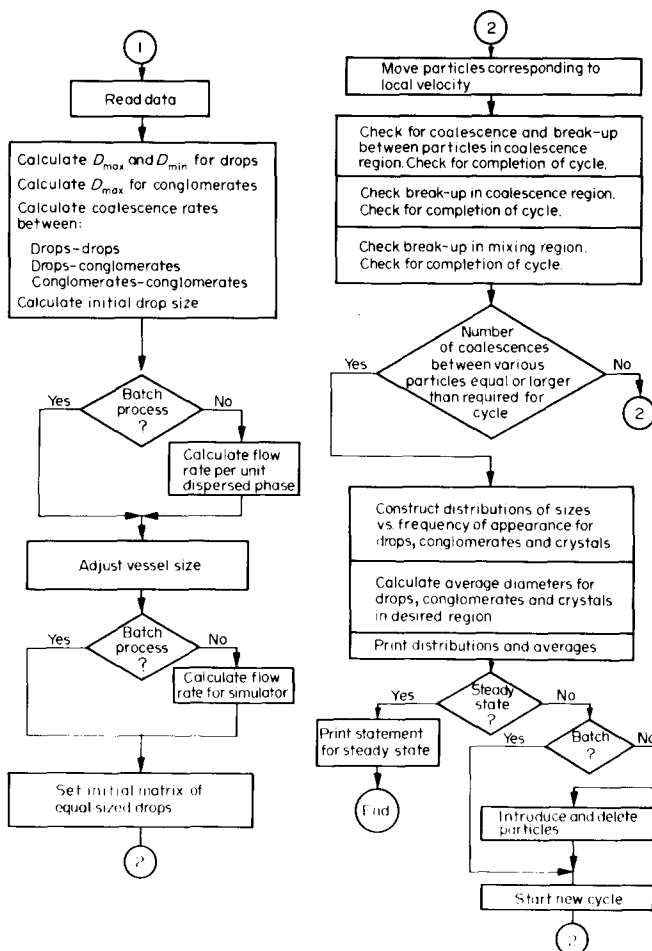


Figure 2. General flow chart for the simulation model.

RESULTS AND DISCUSSION

The calculated results were compared to the following experimental data which appear in the literature.

(a) Batch systems

1. Shiloh (1970): water dispersion in kerosene,
2. Brown & Pitt (1972): kerosene dispersed in water,
3. Vermeulen *et al.* (1955): water dispersed in kerosene,
4. Sprow (1967): isobutyl ketone dispersed in salt water.

(b) Continuous systems

5. Setzer & Treybal (1963): isobutanol dispersed in water,
6. Shiloh *et al.* (1970, 1975): aqueous solution of Na_2SO_4 dispersed in kerosene.

As seen from figures 3–6 the difference between the calculated and the experimental results for the batch systems is smaller than 20%. The difference for the continuous system, figure 7, was within 25%. The latter is probably due to the fact that some experimental data were obtained before the systems reached dynamic equilibrium.

It is important to note that the agreement between the calculated and experimental results hinges upon the proper choice of the numerical constant K in [1]. This value is characteristic of the experimental system under consideration and must be determined experimentally for each system under consideration. The values, calculated independently for each systems, are summarized in Table 1.

Table 1. Summary of the proportionality coefficient K used to calculate the maximum diameter in [1]

Reference	Type of system	K Values
Shiloh (Batch) (1970)	Water in kerosene	0.972
Brown & Pitt (Batch) (1972)	Kerosene in water	0.972
Vermeulen (Batch) (1955)	Water in kerosene	0.261
Sprow (Batch) (1967b)	Iso-butyl ketone in salt water	1.898

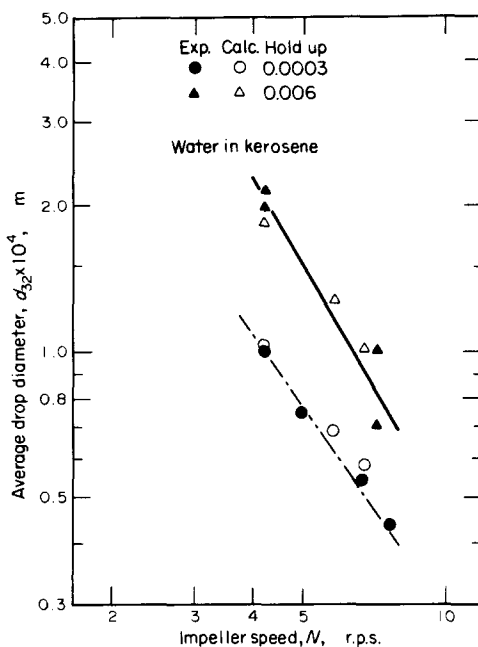


Figure 3. Comparison of simulated data and experimental data of Shiloh (1970). Mean drop diameter vs. impeller speed.

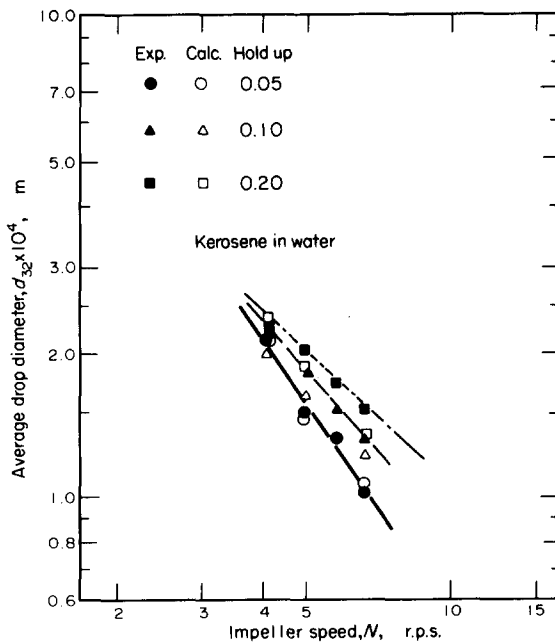


Figure 4. Comparison of simulated data and the experimental data of Brown & Pitt (1972). Mean drop diameter vs. impeller speed.

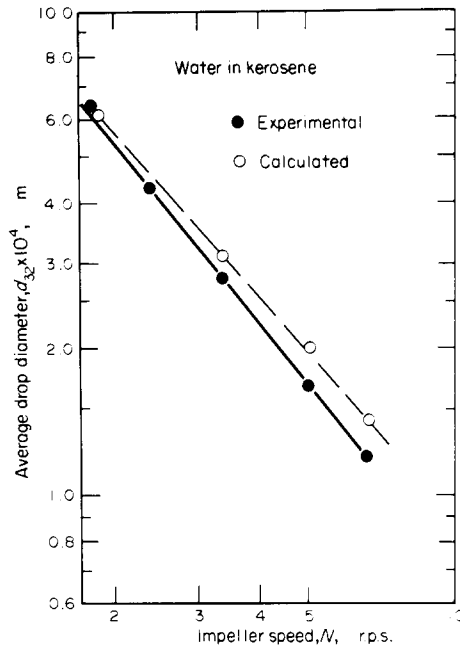


Figure 5. Comparison between simulation model and Vermeulen's (1955) experimental data. Mean diameter vs. impeller speed.

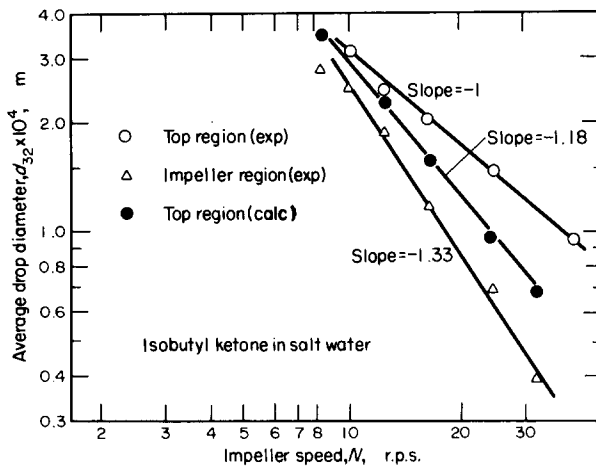


Figure 6. Comparison of Sprow's experimental results (1967) with simulated results. Average drop diameter vs. impeller speed.

Although it is probably safe to assume that the proportionality coefficient is some function of the physical properties of the system, available data are insufficient to determine this proportionality factor independently without reference to an experimental system.

As seen from figures 3–6, the average drop size decreases with the increase in the impeller velocity. Also, the average drop size increases with the increase of the dispersed phase hold-up. With reference to figure 6, it is interesting to note that the simulation model, which assumes two major regions in the container (a mixing region and a coalescence region), yields results which correspond to the average of the experimental results which were measured in the two regions in the container (the mixing region and the 'dead' coalescence region).

Although numerous studies have been conducted in continuous dispersed phase systems, only a few report data suitable for comparison to this model. Inspection of the data of Setzer & Treybal (1963) shows that where the residence time of the fluids in the container is relatively long,

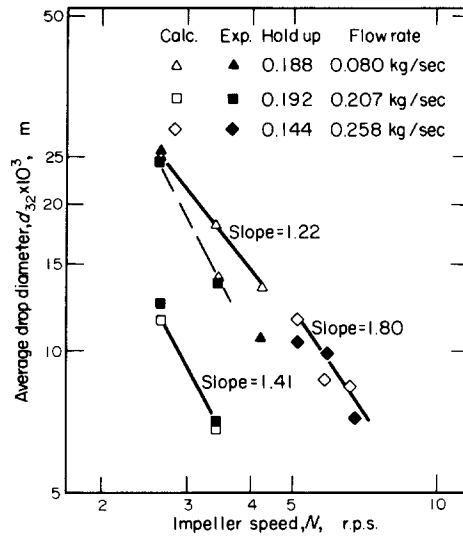


Figure 7. Comparison of impeller speed effect on average drop diameter in Setzer & Treybal's work (1963) and the simulation model.

i.e. low flow rates (0.080 kg/sec), the average drop size dependence on the impeller's velocity is similar to the batch system (slope of -1.22 for the continuous system as compared to -1.2 for the batch system). However, as the residence time decreases (flow rate of 0.239 kg/sec) the dependence of the average drop size on the flow rate increases.

With reference to figure 7, it is noteworthy that the presentation of the data for $\phi = 0.192$ of Setzer & Treybal (1963) is probably erroneous (there seems to be a disagreement between their reported average drop sizes and the values calculated from the experimental specific area data), and the data presented here is based on recalculating the sizes from the original experimental data.

McCoy & Madden (1969) studied the time dependence of the drop size distribution. Figure 8 represents the experimental unsteady distribution and the steady state distribution calculated in this work. Obviously, care must be exercised when data are collected from continuously operating systems.

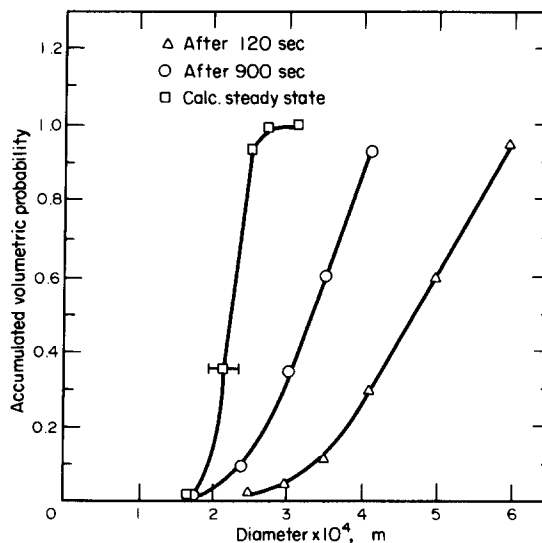


Figure 8. Experimental results of McCoy & Madden (1969) for unsteady distribution vs. steady state simulated distribution.

Testing the model for the three-phase system was somewhat limited due to the absence of semi-empirical correlations for the functional relationships between the many parameters of the system. The comparison was based on the scanty experimental values and quantitative assumptions reported by Shiloh *et al.* (1973). The agreement between the calculated results and the experimental data shown in figure 9 is quite satisfactory.

Though testing the model by relating to real systems and available experimental data is satisfactory, the analysis brings out the need for additional experimental data from which the functional relationships between the various parameters in the system can be reliably obtained. As a direct consequence of this study it is recommended that additional data be obtained for an extended analysis of the three-phase systems. In particular, data relating the size of the conglomerates and the coalescence rate between drops and conglomerates as a function of the various operating parameters are required. Nucleation and crystal growth rate data for different systems are also needed for reliable description of three-phase systems.

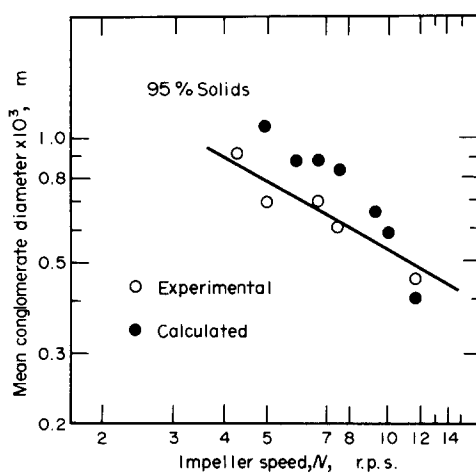


Figure 9. Impeller speed effect on conglomerate size. Comparison of Shiloh's (1973) experimental data with simulated data.

CONCLUSION

A relatively simple simulation model for two and three-phase systems has been developed. The model successfully describes the hydrodynamic characteristics of the two and three-phase systems and can accommodate additional data and correlations to predict the kinetics and crystallization in three-phase crystallizers. However, additional work is required to obtain such data.

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BROWN, D. E. & PITT, K. 1972 Drop size distribution of stirred non-coalescing liquid-liquid system. *Chem. Engng Sci.* **27**, 577-583.

CHEN, H. T. & MIDDLEMAN, S. 1967 Drop size distribution in agitated liquid-liquid system. *A.I.Ch.E. JI* **13**, 989-995.

HILLESTAD, J. G. & RUSHTON, J. H. 1966 Symposium on Coalescence 59th National Meeting 22b.

HINZE, J. U. 1955 Fundamentals of the hydrodynamic mechanism of splitting in dispersion processes. *A.I.Ch.E. JI* **1**, 289-295.

LEVICH, V. G. 1962 *Physicochemical Hydrodynamics*. Prentice Hall, New York.

- LOVE, J. R. 1965 Drop sizes in liquid-liquid dispersions in mixing tanks. M.Sc. Thesis, Purdue University.
- McCOY, B. J. & MADDEN, A. J. 1969 Drop size in stirred liquid-liquid systems via encapsulation. *Chem. Engng Sci.* **24**, 416-419.
- MLYNEK, Y. & RESNICK, W. 1972 Drop sizes in an agitated liquid-liquid system. *A.I.Ch.E. Jl* **18**, 122-127.
- SETZER, H. J. & TREYBAL, R. E. 1963 56th Annual Meeting of A.I.Ch.E. Symp. on Bubble and Drop Phenomena, Preprint 31b.
- SHAH, B. H. & RAMKRISHNA, D. 1973 A population balance model for mass transfer in clear liquid-liquid dispersions. *Chem. Engng Sci.* **28**, 389-399.
- SHILOH, K. 1970 Crystallization in dispersed phase, Ph.D. Thesis (in Hebrew), Technion, Haifa.
- SHILOH, K., SIDEMAN, S. & RESNICK, W. 1971 Hydrodynamic characteristics of dilute dispersed-phase crystallizers. *CEP Symp. Series* **67**, 66-73.
- SHILOH, K., SIDEMAN, S. & RESNICK, W. 1973. Coalescence and break-up in dilute polydispersions. *Can. J. Chem. Engng* **51**, 542-549.
- SHILOH, K., SIDEMAN, S. & RESNICK, W. 1975 Crystallization in a dispersed phase. *Can. J. Chem. Engng* **53**, 157-163.
- SIDEMAN, S., SHILOH, K. & RESNICK, W. 1972 Hydrodynamic characteristics of dispersed-phase crystallizers. 11. Coalescence in three-phase liquid-liquid-solid systems. *I/EC Fundamentals* **11**, 570-578.
- SPIELMAN, L. A. & LEVENSPIEL, O. 1965 A Monte-Carlo treatment for reacting and coalescing dispersed phase systems. *Chem. Engng Sci.* **20**, 247-254.
- SPROW, F. B. 1967a Distribution of drop sizes produced in turbulent liquid-liquid dispersion, *Chem. Engng Sci.* **22**, 435-442.
- SPROW, F. B. 1967b Drop size distributions in strongly coalescing agitated liquid-liquid systems. *A.I.Ch.E. Jl* **13**, 995-998.
- VERMEULEN T., WILLIAMS, G. M. & LANGLOIS G. E. 1955 Interfacial area in liquid-liquid and gas-liquid agitation. *Chem. Engng Prog.* **51F**, 85-94.
- ZEITLIN, M. A. 1970 Description of agitated dispersions with mass transfer and/or reaction. *Ph.D. Thesis*. 111., Inst. of Tech.
- ZEITLIN, M. A. & TAVLARIDES, L. L. 1972 Fluid-fluid interactions and hydrodynamics in agitated dispersions: a simulation model. *Can. J. Chem. Engng* **50**, 207-215.