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DROPLET BEHAVIOUR IN LIQUID/LIQUID EXTRACTION

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CONTENTS

ABSTRACT

The behaviour of liquid/liquid extractors, with special reference to spray columns, pulsed sieve-plate columns and mixer-settlers, has been theoretically and experimentally investigated.

Drops in spray columns can be formed singly or by the break up of jets. Based on 484 data points for 12 liquid/liquid systems from 8 different sources, correlations of drop size have been developed for the single drop and jetting regions in terms of physical properties and nominal nozzle velocity which predict the drop diameter with an average error of 9.7%. A general correlation treating nozzle velocities up to the critical velocity is also presented which predict the drop size with an average deviation of 9.5%.

The concept of slip velocity has been used to correlate the dispersed phase hold-up in spray columns. The drag coefficient defined by Barnea and Mizrahi (1975e) has been modified and slip velocity data in the intermediate zone and lower range of the turbulent zone correlated. The proposed correlation, which predicts two values of hold-up corresponding to loose and dense-packed dispersions, has a practical value of a simple correlation over the relevant range of Reynolds numbers covered.

New correlations to predict dispersed phase hold-up in pulsed sieve-plate columns have been developed in terms of physical properties, operting conditions and column geometry. An analysis of 725 data points for 8 liquid/liquid systems from 5 different sources gave correlations in the absence of mass transfer for mixer-settler, dispersion and emulsion regions, which predict the hold-up with average percentage deviations of 13.5, 12.4 and 13.7 respectively. The break-point between the mixer-settler and dispersion regions is given by the minimum value of the hold-up, and between dispersion and emulsion regions when the dimensionless group $(Af)^3\rho_c/(\lambda\ell\Delta\rho^{3/4}\sigma^{1/4}g^{5/4})$ is equal to 0.05.

Mechanisms of binary coalescence and coalescence at the disengaging interface have been proposed. Based on drop growth and the effect of the thickness of the dense-packed layer on drop/interface coalescence time, models are presented which relate the observations on batch decay profiles to continuous settling. Experimental batch decay data have been correlated by using one of the models and the evaluated parameters used to predict the steady state height in a continuous settler. Good agreement has been achieved between experimental and predicted heights. Finally, an empirical correlation to predict the dispersion band height in a spray column in terms of physical properties and dispersed phase throughput is presented and fairly good agreement between experimental and calculated dispersion band heights obtained.

ZUSAMMENFASSUNG

Das Verhalten von flüssig/flüssig Extraktoren mit speziellem Bezug auf Sprüh- und pulsierende Siebbodenkolonnen sowie Mischer-Abscheider-Kontaktoren wurde theoretisch und experimentell untersucht.

Die Tropfen können in Sprühkolonnen einzeln oder im Strahlzerfall gebildet werden. Aus 484 Messdaten für 12 flüssig/flüssig Systeme von 8 verschiedenen Datenquellen wurden Korrelationen für die Tropfengrösse im Einzeltropfen- und Strahlbereich entwickelt, und zwar in Funktion der physikalischen Eigenschaften und der Durchschnittsgeschwindigkeit in der Düse. Dabei kann der Tropfendurchmesser bis auf 10% genau vorausgesagt werden. Ueberdies wird eine allgemeine Korrelation mit etwa gleicher Genauigkeit angegeben, die die Düsengescwindigkeit bis zur kritischen Geschwindigkeit behandelt.

Mit der Definition der Relativgeschwindigkeit kann der Hold-up der dispergierten Phase in Sprühkolonnen korreliert werden. Der Widerstandskoeffizient nach Barnea und Mizrahi (1975e) wurde nun zu einer Korrelation für die Relativgeschwindigkeit in der Uebergangszone und im unteren Turbulenzbereich modifiziert, womit die Werte des Hold-ups für lockere und dichtgepackte Dispersionen vorausgesagt werden können. Die Korrelation hat Gültigkeit im Reynoldsbereich $Re_{\varepsilon,1} = 7 - 2450$.

Neue Korrelationen sagen den Hold-up der dispergierten Phase in pulsierenden Siebbodenkolonnen voraus in Abhängigkeit der physikalischen Eigenschaften, die Versuchsbedingungen und der Kolonnengeometrie. Es werden 725 Messdaten für 8 flüssig/flüssig Systeme im Mischer-Abscheider-, Dispersions- und Emulsionsbereich analysiert. Die daraus resultierenden Korrelationen geben den Hold-up mit einer durchschnittlichen Abweichung von 13,5, 12,4 und 13,7% an. Der Uebergangspunkt zwischen Mischer-Abscheider- und Dispersionsbereich ist durch das Minimum des Hold-ups bestimmt und zwischen Dispersions- und Emulsionsbereich durch den dimensionlosen Ausdruck $(Af)^3 \rho_c / (\lambda \ell \Delta\rho^{3/4} \sigma^{1/4} g^{5/4})$, der 0.05 wird.

Mechanismen der binären Koaleszenz und der Koaleszenz an der Grenzfläche werden vorgeschlagen. Auf Grund des Tropfenwachstums und des Einflusses des dichtgepackten Schichtanteils auf die Tropfen/Grenzflächen-Koaleszenzzeit werden Modelle für statische Zerfallsprofile und kontinuierliches Ausscheiden präsentiert. Mit einem Modell werden die experimentellen statischen Zerfallsprofile so korreliert, dass die stationäre Höhe im kontinuierlichen Abscheider mit guter Genauigkeit vorausgesagt werden kann. Auch für die Sprühkolonne wurde eine empirische Gleichung ermittelt, um die Dispersionshöhe in Abhängigkeit der physikalischen Eigenschaften und des dispergierten Phasendurchsatzes zu bestimmen.

1. INTRODUCTION

Liquid/liquid extraction is a well-known separation technique that has many applications in petroleum, petrochemical, pharmaceutical, metallurgical and atomic energy industries (Treybal, 1963, Hanson, 1971, Bailes and Winward, 1972). It can be entirely physical in nature - the driving force for mass transfer depending on the difference in relative solubilities among the components of the feed stock and the solvent which has been selected. Many applications in the organic field belong to this category. On the other hand, driving forces can be determined by solubility differences which arise from varying degrees of chemical interaction with the solvent. This is exploited for many metallurgical separations.

The number and variety of liquid/liquid extraction contactors that have been described in the literature are considerable. These can be classified depending whether contact is stagewise or differential, and according to the method used for inducing counter-current flow, such as gravity or centrifugal force. Equipment available includes mixer-settlers (widely used in hydrometallurgy), spray columns and various designs of plate, grid and packed columns. There are also columns with interstage mixing aided by mechanical internal devices (Kühni column, rotating disc contactor, asymmetric rotating disc contactor, Oldshue-Rushton contactor, Scheibel extractor,etc.) or externally applied pulses (pulsed sieve-plate column, pulsed packed column, etc.). A variety of vertical and horizontal centrifugal extractors have also been developed, despite their high cost, and have found fairly wide use in petroleum refining and vegetable oil processing, in addition to the production of antibiotics (Logsdail and Lowes, 1971, Bailes and Winward, 1972).

Design methods of established contactors are becoming more sophisticated and some new devices (EC column, SHE column,etc.) which might help to extend the field of liquid/liquid extraction have appeared. Rapid developments in both the theory and practice of liquid/liquid extraction equipment are continuing, although considerable areas of ignorance remain. Even today, pilot scale experimentation is normally an inevitable preliminary to full scale design for any new process.

Since there is a wide variety of contactors to choose from for any particular process, several design considerations and process parameters have to be considered before making a final choice. One of the important calculations to be done in a design procedure is the number of theoretical stages, either analytically or graphically. All types of extractors can be used satisfactorily when few, say two or three, theoretical stages are required ; when more than this, perhaps ten or twenty, are needed then the choice becomes difficult. Generally speaking, columns are used when the number of stages required is less than about three to six, although for very low throughputs and low axial mixing effects a higher number of stages can be accommodated (Arnold, 1974). Therefore, when the required number of equilibrium stages is more than this, columns may be eliminated, although not so the centrifugal units that may be staged. The latter have a high capital cost and are only used for special applications such as a very low density difference between phases, or when a very short residence time is specified to minimize solvent degradation.

For low and moderate throughputs a spray or packed column could be used; for intermediate and high throughputs mechanically agitated columns or mixer-settler units could be employed. For high throughputs the effect of scale on factors such as axial mixing in columns is largely a matter of experience, design methods being inadequate (Oldshue, 1974). These problems do not occur with mixer-settlers, although entrainment can be a problem. For high throughputs columns are still preferable because of the economies they offer with respect to agitation energy, floor space and inventory, although for very large diameters axial mixing may account for a significant proportion of the total column height needed.

The physical properties of the process fluids will also influence the choice. The density difference is very important, since low values reduce the dispersed phase velocity in the column, or, with mixer-settlers, in the settling chamber and thus reduce the throughputs. Practically, a settler will perform with density differences as low as 10 kg/m^3, but its size then becomes very large in relation to the mixing tank for a given throughput (Glasser et al., 1976). The drop size in extractors is a function of interfacial tension and high values of interfacial tension correspond to large drops (small interfacial area) and hence poor mass transfer performance. However, a high interfacial tension is not a serious restriction when a mechanically agitated contactor is used, since the performance can be improved by increasing the power input to the system. Systems with low interfacial tension can not be subjected to high shear or turbulence forces without stable emulsions being formed. Unagitated columns may suit the purpose very well, although gentle agitation could be arranged in an agitated contactor. The viscosities of the phases may also be of importance if appreciably high, and in such cases experiments should be carried out with the actual system under consideration.

When solids are present in one or both of the phases many types of contactor are liable to blockage and require dismantling for cleaning. Exceptions are the pulsed sieve-plate and reciprocating-plate columns which are self-cleaning to a considerable extent. In the case of mixer-settlers a shut-down for cleaning is relatively simple.

Other considerations affecting selection might be the floor area and/or headroom available, peculiar reaction kinetics requiring high turbulence or long residence time, and materials of construction.

1.1 Scope

It is very useful to synthesise the results of the available studies on drop size, dispersed phase hold-up, and axial mixing and mass transfer coefficients so as to simulate, from first principles, the overall performance of a piece of equipment. A simulation model allows designs to be carried out with confidence for systems which have not been previously handled in the equipment under consideration. However, there have been relatively few attempts, primarily because the available information is either incomplete or conflicting and confusing.

In Chapter 4 of this work new correlations have been suggested for the published experimental results on the drop size in spray extraction columns, and the dispersed phase hold-up in spray and pulsed sieve-plate extraction columns. Predictions of various correlations that are available in the literature (Chapter 2) to describe the above-mentioned parameters are compared with these experimental results and the inadequacy of most of the correlations is deomonstrated.

Another practical problem which arises subsequent to the mass transfer and is particularly important for multistage processes in which stage-wise equipment is used, is the physical separation of a liquid/liquid dispersion into extract and raffinate phases. Unless this can be accomplished easily and nearly completely, the extraction process is of little value. The gravity settler which is widely used for this purpose consists essentially of a vessel to which the dispersion is continuously fed,and from which the two phases are discharged with anticipated complete separation.

The mechanism of this apparently very simple operation has not been very well understood. Very few experimental or theoretical investigations have appeared in the literature. As a result, the approach to the design is largely empirical and in many cases the industrial settlers are grossly oversized. In operations involving many stages the settlers and their inventory represent an important immobilization of capital.

It is known that the coalescence properties of liquid phases containing organic commpounds and used in closed systems may change with time due to many different reasons: chemical reactions (such as oxidation), differential losses of volatile components, interactions with the construction materials of the container, crud produced by organic liquid-borne fungi, air or water-borne bacteria,etc. Thus the experimentation and even the concept of steady state are much more complicated, which explains the fact that there are relatively few investigations in the field of phase separation.

A worthwhile goal of the fundamental study of settling mechanism is to reduce the scale of pilot work and cost involved by attempting to predict continuous settler capacity on the basis of a relatively small-scale batch test. Since a batch test is inexpensive and the simplest way of obtaining the relevant information, effort must therefore be put into a more fundamental understanding of the relation between batch and continuous settling. A set of batch tests over a wide range of initial conditions covering all the variables of a liquid/liquid system (dispersion height, drop size distribution, phase ratio, etc.) should contain all the information required to design a continuous settler.

Models based on drop/drop and drop/interface coalescence relating the batch and continuous settling are presented in Chapter 6 and a fairly good agreement between continuous results and those calculated from the batch settling experiments is also obtained. Finally, a correlation for the prediction of the steady state band thickness in a spray column in terms of physical properties of the liquid pairs is given.

2. DROP DYNAMICS

The motion of liquid drops and their behaviour in another liquid medium of infinite or restricted extent is of importance in liquid/liquid extraction processes, since in extraction equipment the contact between the phases is achieved through dispersion of one of the phases as drops. Hence a knowledge of the hydrodynamic aspects should provide the basic information needed for the design of liquid/liquid contactors in which the drop size is related to the transfer efficiency and the terminal velocity to the capacity of the equipment.

2.1 Drop Formation from Nozzles and Orifices

The knowledge of the interfacial area formed when one liquid is injected into a second immiscible liquid through single or multiple openings is necessary for the calculation of heat and mass transfer rates in such processes.

At low nozzle velocities the drop is formed at the tip of the nozzle. Above a certain velocity a jet is formed which breaks up into drops. The jet length increases with increasing velocity till a critical value is reached, beyond which the jet length again decreases. The maximum jet length often corresponds to a minimum drop diameter (Keith and Hixson,1955, Skelland and Johnson, 1974). Finally, at still higher velocities, the jet length shrinks to zero and the drops are again formed at the tip of the nozzle - this is the atomisation region.

2.1.1 Single Nozzles and Low Velocities

Harkins and Brown (1919) derived an expression for predicting the static drop volume by equating the buoyancy and interfacial tension forces and correcting the volume for the fraction of liquid which remains attached to the nozzle after drop break-off:

$$V_D = \frac{\chi \pi \sigma d}{g \Delta\rho} \tag{2.1}$$

where χ is the so-called Harkins-Brown correction factor.

For cases where velocity effects become important, Hayworth and Treybal (1950) were among the first to provide a correlation. Their equation in cgs units is as follows :

$$V_D + 4.11\mathrm{x}10^{-4}\, V_D^{2/3} \left(\frac{\rho_d\, v^2}{\Delta\rho}\right) = 21\mathrm{x}10^{-4} \left(\frac{\sigma d}{\Delta\rho}\right) + 1.069\mathrm{x}10^{-2} \left(\frac{d^{0.747} v^{0.365} \mu_c^{0.186}}{\Delta\rho}\right)^{3/2} \qquad (2.2)$$

These authors also provided a chart to eliminate the necessity of trial-and-error computation for the drop volume.

Null and Johnson (1958) found maximum average errors of 94 and 377% when they compared their experimental results with their own correlation and that of Hayworth and Treybal, respectively. Meister (1966) also found that the Hayworth-Treybal and Null-Johnson correlations did not satisfactorily predict the drop size over the wide range of liquid properties and nozzle sizes he had studied.

Rao et al. (1966) developed a correlation based on a two-stage drop formation process. In the static stage the drop inflates till the bouyant force overcomes the interfacial tension force (Harkins-Brown drop volume). During the second stage the drop continues to grow until it detaches from the nozzle. These authors claimed that their analysis significantly reduced the error for many liquid/liquid systems. Scheele and Meister (1968a) gave an improved correlation for the drop volume, based again on a two-stage drop formation process, and showed that their analysis was more accurate than the Hayworth-Treybal and Null-Johnson correlations and could be used for a wide range of physical properties and nozzle diameters.

In the last decade the important contributors to the field were de Chazal and Ryan (1971), Izard (1972) and Kagan et al. (1973). Table 2.1 summarizes the important correlations for the formation of drops at low nozzle velocities from single nozzles. (In this table Bühler's (1977) simplification of Izard's (1972) somewhat

Table 2.1 Correlations Predicting the Volume of Drops Produced from Single Nozzles at Low Velocities

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Scheele and Meister (1968a):

$$V_D = \chi\{\frac{\pi d\sigma}{\Delta\rho g} + \frac{5\mu_c \pi d^3 v}{\phi^2 \Delta\rho g} - \frac{\rho_d \pi d^2 v^2}{3\Delta\rho g} + 4.5(\frac{\sigma\pi^2\rho_d d^6 v^2}{16(\Delta\rho)^2 g^2})^{1/3}\}$$

where $\phi = (6V_D/\pi)^{1/3}$

de Chazal and Ryan (1971):

$$V_D = \frac{\pi d\sigma}{\Delta\rho g}\{\chi + 1.648\,\frac{g\Delta\rho d\ v\ V_D^{1/3}}{2\sigma\ U} - 0.857\,\frac{d\rho_d v^2}{2\sigma}(1 + \upsilon)\}$$

where $\upsilon = 0$ for $(\rho_d d\ v^2/2/\sigma)^{1/2} \le 1.07 - 0.75(\Delta\rho g d^2/4/\sigma)^{1/2}$

otherwise,

$$\upsilon = 0.286(\Delta\rho g d^2/4/\sigma)^{1/2}$$

Izard (1972):

$$V_D = \frac{1}{\Delta\rho g}\{\pi d\sigma + \frac{\pi d\ v\mu_c}{2}(\frac{\mu_c + 1.5\mu_d}{\mu_c + \mu_d}) - \frac{\pi d^2 v^2 \rho_d}{3}(1 - \frac{2\rho_d}{2\rho_d + \rho_c})\}$$

Kagan et al. (1973):

$$V_D = \frac{\chi\pi\ d\sigma}{\Delta\rho g}(1 + 2.39\,\frac{d}{(8\sigma/\Delta\rho/g)^{1/2}}\,W^{1/3} - 0.485W)$$

where $W = \frac{(\rho_c + \rho_d)\ dv^2}{2\sigma}$

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complicated correlation is given). The calculation of drop diameter using the correlation of Scheele and Meister (1968a) is iterative when the continuous phase viscosity exceeds 10 mPa s but not when the viscosity is less than this since the drag term is then negligible. de Chazal and Ryan's (1971) correlation is complex because it requires the terminal velocity U to be calculated as a function of drop diameter using Hu and Kintner's (1955) or Klee and Treybal's (1956) correlations. (See Section 2.3.1 for correlations of terminal velocities of single drops). The equations of Izard (1972) and Kagan et al. (1973) are simple to handle since a trial-and-error solution is not required.

The Harkins-Brown correction factor in equation (2.1) and Table 2.1 can be calculated using a diagram published by Scheele and Meister (1968a) or approximated by the equation of Horvath et al. (1978) :

$$\chi = 0.6 + 0.4 \exp\{-2d(\frac{\Delta\rho g}{\pi\sigma d})^{1/3}\} \qquad (2.3)$$

2.1.2 Jet Break-up from Single Nozzles

As already stated, with higher nozzle velocities a jet issues from the nozzle and the drops are formed by its disintegration. There is, however, a serious lack of reliable correlations for the prediction of drop diameter in the jetting region and most of the studies directed toward understanding jet break-up are concerned with the determination of nozzle velocity when jetting starts (minimum jetting velocity) and the velocity with maximum jet length (critical velocity).

The work of Hayworth and Treybal (1950) was largely devoted to the single drop region with a few runs in the incipient jetting region. From observations on 14 liquid/liquid systems these authors found that a jet normally formed when the nozzle velocity reached about 0.1 m/s, but made no attempt to define the jetting velocity precisely. Ruff et al. (1976) and Ruff (1978) recently proposed :

$$v_j = (\frac{2\sigma}{\rho_d d})^{1/2} \qquad (2.4)$$

where v_j is the minimum jetting velocity. Other pertinent correlations predicting v_j are given in Table 2.2.

Several papers are available on the critical nozzle velocity. Smith and Moss (1917) found the critical velocity, v_c, to be independent of the dispersed phase viscosity and proportional

Table 2.2 Correlations Predicting the Minimum Jetting Velocity

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Fujinawa et al. (1957):

$$v_j = 1.75\text{x}10^{-2}\ \sigma^{0.20}\ d^{-0.50}$$

Shiffler (1965):

$$v_j = 1.97\left(\frac{\sigma}{\rho_d\ d}\right)^{0.50} \left\{1 - \frac{0.64\ d^{0.78}(g\Delta\rho)^{0.39}}{\sigma^{0.39}}\right\}^{0.50}$$

Scheele and Meister (1968b):

$$v_j = \left\{3\left(\frac{\sigma}{\rho_d\ d}\right)\left(1 - \frac{d}{\phi}\right)\right\}^{0.50}$$

de Chazal and Ryan (1971):

$$v_j = \left(\frac{2\ \sigma}{\rho_d\ d}\right)^{0.50} \left\{1.07 - 0.75\left(\frac{\Delta\rho g d^2}{4\sigma}\right)^{0.50}\right\}$$

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to $(\sigma/\rho_d/d)^{1/2}$, the costant of proportionality being between 2 and 3. Tyler and Watkin (1932) correlated the critical velocity by two dimensionless groups, $v_c(\rho_d\ d/\sigma)^{1/2}$ and $(\sigma\ \rho_c d/\mu_c^2)^{1/2}$. Keith and Hixson (1955) observed that the drop sizes were much more uniform below the critical velocity than for those above. Ranz (1958) suggested that the following equation could be used for the prediction of critical nozzle velocity :

$$v_c = 2.83\left(\frac{\sigma}{\rho_c\ d}\right)^{0.50} \qquad (2.5)$$

From the analysis of Keith and Hixson's (1955) data, Hughmark (1967) suggested :

$$v_c = 2.94 \left(\frac{\sigma}{\rho_d \, d}\right)^{0.50} \qquad (2.6)$$

Combining this equation with equation (2.4) shows that $v_c \simeq 2v_j$ as suggested by Ruff (1978).

The critical velocity and the corresponding critical drop diameter can also be calculated by using the equations given by Treybal (1963) :

$$v_c = 0.90 \left(\frac{\phi_c}{d}\right)^2 \left(\frac{\sigma/\phi_c}{0.5137 \ \rho_d + 0.4719 \ \rho_c}\right)^{1/2} \qquad (2.7a)$$

$$\frac{\phi_c}{d} = 2.07 \ \frac{1}{0.485 E\ddot{o} + 1} \qquad \text{for} \quad E\ddot{o} < 0.615 \qquad (2.7b)$$

$$\frac{\phi_c}{d} = 2.07 \ \frac{1}{1.51 E\ddot{o}^{1/2} + 0.12} \qquad \text{for} \quad E\ddot{o} > 0.615 \qquad (2.7c)$$

where $E\ddot{o} = \Delta\rho g \ d^2/\sigma$. Equations (2.7b,c) predict a minimum average drop diameter.

Although the correlation of de Chazal and Ryan (see Table 2.1) does not extend to the critical nozzle velocity it may still be used to calculate the drop diameter in part of the jetting region when the following inequality given by the same authors is satisfied :

$$\frac{v}{\sqrt{gd}} \leq 2.16 \left(\frac{\sigma}{\Delta\rho g \ d^2}\right)^{0.95} \left(\frac{\Delta\rho}{\rho_d}\right) \qquad (2.8)$$

Jetting conditions received the major emphasis in the investigation of Skelland and Johnson (1974). For the 6 liquid/liquid systems they studied the ratio of the critical drop diameter to the critical jet diameter varied between 1.8 and 2.6, the mid-point of the range being 2.2 (the value of 2.2 differs slightly from 2.07 reported by Christiansen and Hixson (1957)). These authors have given a calculation scheme to determine the drop diameter in the jetting region which involves the calculation of the critical velocity using equations (2.7a-c). The critical velocity so computed is then used to calculate the dimensionless nozzle velocity, v/v_c, which in turn is required in a graph given by them to determine the dimensionless drop diameter, ϕ/d_{jc}; the critical jet diameter d_{jc} is obtained from equations (2.7b,c), replacing ϕ_c by $2.07d_{jc}$ and finally the actual drop diameter.

2.1.3 Multiple Nozzles

When drops are formed from a set of nozzles, adjacent nozzles may affect the drop size formed at any single nozzle. It is therefore important to consider the pitch and arrangement of nozzles on the distributor plate. At low flow rates of the dispersed phase not all the nozzles are in operation; moreover, the drop size formed can be several times the nozzle size and if the nozzles are not set sufficiently wide apart, growing drops may touch each other and coalesce. In the jetting region interference among the adjacent jets due to the "weaving" of the jets could also affect the drop size.

If the drops are formed by a perforated plate and the plate material is wetted by the dispersed phase, at low nozzle velocities the dispersed phase not only wets the orifice perimeter but also spreads over a wider surface resulting in the formation of non-uniform large drops without any reproducibility (Perrut and Loutaty, 1972). According to Ruff et al. (1976) and Mersmann (1977) the seeping of the continuous phase through the orifices in a perforated plate can be avoided and drop formation from all the orifices is secured if the dimensionless group $v^2\, d\, \rho_d/\sigma$ is greater than 2.

Perrut and Loutaty (1972) formed drops using 12 different perforated plates. For the 15 liquid/liquid systems investigated the average drop size was linearly related to the Eötvös number in the jetting region :

$$\frac{\bar{\phi}}{d} = 2.07\ (1 - 0.193\text{Eö}) \qquad (2.9)$$

Vedaiyan (1969) studied the drop formation for 4 liquid/liquid systems using 7 different distributors with nozzle sizes of 1 to 4.75 mm. He found that the drop size produced by multiple nozzles decreased exponentially with the nozzle velocity and continued to decrease even beyond the critical velocity. A correlation was proposed for the prediction of the Sauter mean drop diameter given by :

$$\phi_{32} \left(\frac{\Delta\rho g}{\sigma}\right)^{1/2} = 1.592\left(\frac{v^2}{2gd}\right)^{-0.0665} \qquad (2.10)$$

Miller and Pilhofer (1976) experimentally investigated the drop formation for the toluene/water system using perforated plates with a large number of orifices (195-5910). They found that at low flow rates of the dispersed phase (single drop region), the drops were smaller than those formed from single nozzles and gave the explanation that at low flow rates not all the orifices operate and the active orifices in fact operate near jetting velocity. When all orifices operated (jetting region) the drop formation from each orifice of the perforated plate was like that from a single nozzle of the same size; the drop diameter decreased with increasing nozzle velocity and reached a minimum (corresponding to the critical velocity) and began to increase beyond the critical velocity.

Horvath (1976) used multiple nozzles of 1 mm diameter and 10 mm length, arranged on a triangular pitch of 7 mm. His data on the o-xylene/water system shows an S-shaped variation of the drop size with the nozzle velocity. Based on his data, Horvath et al.(1978) suggested an empirical equation for the jetting region which correlates the Sauter mean drop diameter with variables v_c and ϕ_c given by equations (2.7a-c). The final form of the equation is :

$$\frac{\phi_{32}}{\phi_c} = \frac{v_c}{v} + 0.71 \log_e\left(\frac{v}{v_c}\right) \qquad (2.11)$$

2.2 Liquid/Liquid Dispersions in Stirred Vessels

In a stirred vessel two immiscible liquids are agitated so as to disperse one of them into fine droplets of large interfacial area. Forces produced by turbulent fluctuations and viscous friction tend to break up the droplets, whereas collisions among drops may result in coalescence. When the agitation is maintained under constant conditions a dynamic equilibrium between break-up and coalescence processes is obtained. The characteristics of a droplet dispersion depend on the geometry and size of the mixer and its construction material, the intensity of agitation, phase ratio and the physical properties of the liquid/liquid system.

In addition to the information on mass transfer coefficients and interfacial area, a knowledge of further operating parameters such as the minimum impeller speed for complete dispersion, phase inversion ratio and scale-up behaviour is very important.

2.2.1 Minimum Impeller Speeds for Complete Dispersion and Uniform Dispersion

The minimum impeller speeds for both complete and uniform dispersion should be known to enable efficient design of the mixing tank. Complete dispersion refers to a situation in which no large drops or agglomerates of drops are found on the bottom of the mixing tank or at the liquid surface. On the other hand, uniform dispersion describes a situation in which the concentration of droplets is constant throughout the mixing tank.

Nagata et al. (1950) performed a limited study on liquid/liquid systems in an unbaffled, flat-bottomed cylindrical vessel using a centrally mounted, four-bladed paddle with a T/D of 3, a blade width of 0.06T and liquid height equal to the vessel diameter. The following empirical correlation was proposed :

$$N_m = 6D^{-2/3} \left(\frac{\mu_c}{\rho_c}\right)^{1/9} \left(\frac{\Delta\rho}{\rho_c}\right)^{0.26} \qquad (2.12)$$

where N_m is the minimum impeller speed for complete mixing.

It follows from equation (2.12) that N_m is independent of interfacial tension and dispersed phase viscosity.

van Heuven and Beek (1971) investigated the design and scale-up rules for power input, drop size and minimum impeller speed for complete dispersion using 7 different baffled cylindrical tanks with turbine impellers. They gave the following correlation for N_m for the 4 liquid/liquid systems they studied :

$$\frac{N_m^2 D}{g} = 22\left(\frac{N_m D^2 \rho_c}{\mu_c}\right)^{-3/5} \left(\frac{\mu_c^2}{\rho_c \sigma D}\right)^{-1/5} \left(\frac{\Delta\rho}{\rho_c}\right)(1 + 2.5\varepsilon)^{7/3} \qquad (2.13)$$

It follows from the above equation that for scale-up, $N_m^{2.6} D^2$ should be kept constant.

Skelland and Seksaria (1978) observed six distinct types of mixing phenomena in an experimental study of the minimum impeller speeds required for complete dispersion in baffled mixing tanks. The variables investigated were size, location and form of impeller and the physical properties of 5 equal-volume liquid/liquid systems. They correlated 195 results with the following expression :

$$N_m = C_{2.1} D^{m_{2.1}} \mu_c^{1/9} \mu_d^{-1/9} \sigma^{0.3} \Delta\rho^{0.25} \qquad (2.14)$$

The constant $C_{2.1}$ and index $m_{2.1}$ depend upon the type of impeller and position of impeller in the mixing tank.

As pointed out earlier, complete dispersion refers only to the elimination of separate layers, without regard to uniformity of mixing. Pavlushenko and Ianishevskii (1958) defined the minimum impeller speed for uniform dispersion, N_u, as the number of revolutions per unit time at which the relative concentration of the dispersed phase reaches 100 percent over the entire stirred volume. These authors performed experiments on 15 liquid/liquid sytems using glass vessels of standardized spherical bottoms and gave correlations to estimate N_u for propeller and turbine agitators in baffled as well as unbaffled vessels.

Their important conclusions were :

1) phase ratio has no effect on N_u;
2) N_u increases with increasing vessel diameter if the baffles are present, but is independent of vessel diameter in the absence of baffles;
3) N_u decreases with decreasing distance of the impeller from the bottom of the vessel.

Skelland and Lee (1978) used the mixing index developed by Hixson and Tenney (1935) and defined the minimum speed of the impeller for uniform mixing as the rotational speed that is just sufficient to give a mixing index of 98%. According to these authors, this condition corresponds to gross uniformity of the proportions of dispersed to continuous phase in all sampled parts of an agitated vessel. Further, all droplets are not necessarily equally sized or equally spaced in this state. Their experimental results of 5 equal-volume liquid/liquid systems (same as those used by Skelland and Seksaria (1978)) were again correlated by equation (2.14), the values of N_u being about 8% greater than N_m on the average.

2.2.2 Phase Inversion

The identification of the dispersed phase under all conditions and the limits of stability of dispersions are very important in solvent extraction operations. Phase inversion is the transition from one phase dispersed to the other. It is generally represented graphically by plotting the volume fraction of the dispersed phase in an heterogeneous mixture at inversion against the impeller speed. Figure 2.1 depicts a phase diagram which is typical of agitated heterogeneous liquid/liquid systems (Luhning and Sawistowski, 1971, Arashmid and Jeffreys, 1980). Such an inversion characteristic demonstrates the existence of a hysteresis effect, represented graphically by two curves defining an ambivalent region. The system can only exist as aqueous dispersed/organic continuous above the upper curve, and as organic dispersed/aqueous continuous below the lower

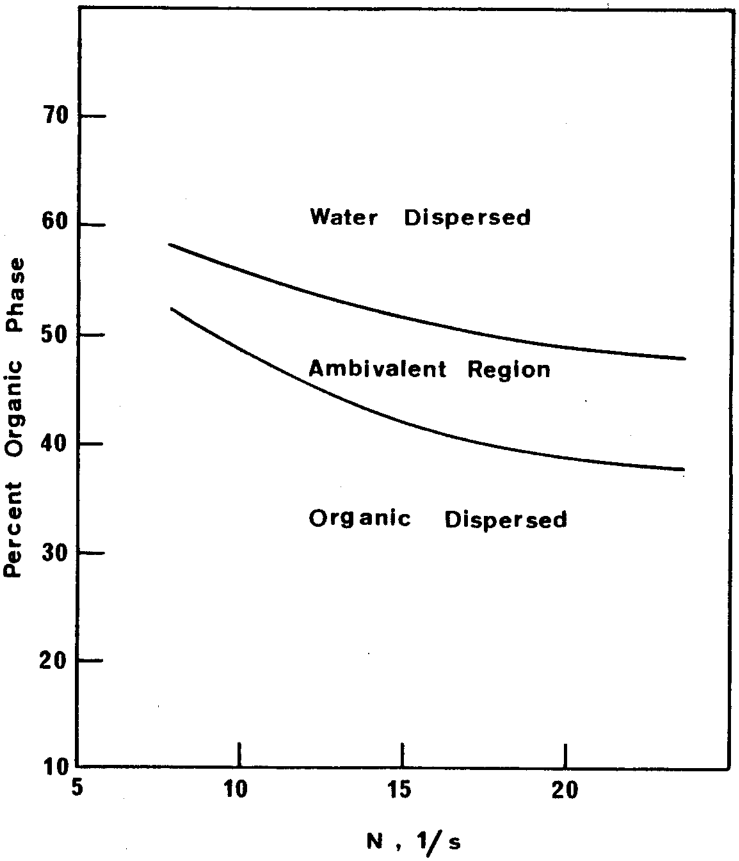


Figure 2.1 Typical Inversion Characteristics for Oil/Water Dispersion

curve. In between the two curves either aqueous or organic dispersed dispersions can be maintained, and in this region spontaneous phase inversion can take place.

Since considerations of plant performance usually dictate operation within the ambivalent region, it is necessary to be able to predict the ambivalent range and the phase inversion concentrations. Phase inversion may lead to sudden increases in phase entrainments and flooding in gravity settlers (Rowden et al., 1975).

From a geometric viewpoint the drops of one phase in another would remain dispersed until they occupied approximately 74% of the total volume (close packing). Any further addition of the drop phase would lead to distortion of the drops with the resultant forces leading to thinning of the continuous phase films and, provided no other forces were present, eventually to coalescence. In this situation the shock of two drops coalescing might well be sufficient to cause other drops to coalesce, leading to phase inversion.

Even though the energy released on coalescence is small it is in fact released over a very short time (Levich, 1962) possibly giving rise to quite an intense pressure wave. This might well be the reason why phase inversion appears to occur so suddenly.

Forces of attraction or repulsion between the drops or between the drop and a surface could significantly alter this static picture and in this respect one would expect surfactants to play an important part. Viscosity could have a significant damping effect on the rate of coalescence, due both to the rate of thinning of the continuous phase film and the rate of coalescence of the dispersed phase. Other factors which may influence phase inversion include the density difference between the two phases, interfacial tension and agitator speed. Impeller position, number and shape, geometry of the mixing tank,and finally temperature, owing to its effect on the physical properties of the stirred liquids, may also be effective on phase inversion.

Rodger et al. (1956) in a study of the interfacial area in concentrated dispersions reported some qualitative observations on phase inversion. They found that at low rates of energy input the stable dispersion was oil-in-water, but as the energy input rate was increased the dispersion would invert to water-in-oil. They also observed that phase inversion occurred more readily in systems in which the ratio of the difference in densities to the continuous phase density ($\Delta\rho/\rho_C$) was large.

Quinn and Sigloh (1963) dealt with phase inversion in mixing immiscible liquids and found that the volume fraction of the organic phase at phase inversion decreased with increasing impeller speed and became independent of the stirring speed at speeds 2 to 3 times the minimum speed for complete dispersion. They also observed that a water continuous dispersion resulted if the impeller was placed entirely in the water phase and, correspondingly, an organic continuous dispersion could be obtained by placing the impeller in the organic phase.

Yeh et al. (1964) found that temperature, interfacial tension and density had no effect on points of inversion. According to their volume-viscosity relationship the phase-volume ratio at the point of inversion is equal to the square root of the interfacial viscosities of the respective phases.

Selker and Sleicher, (1965) studied factors affecting the dispersion of two immiscible liquids. The variables investigated were viscosities, densities, impeller speed, manner of initiating the dispersion and the construction materials of the mixing apparatus. They concluded that the range of volume fraction within which either of the two immiscible liquids could be dispersed depended mainly on the viscosity ratio of the liquids; as the viscosity of a phase increased, its tendency to be dispersed increased. Within the ambivalent range the phase that was dispersed depended upon the mixing procedure.

Luhning and Sawistowski (1971) found that interfacial tension is one of the main factors affecting the width of the ambivalent region. They gave an empirical correlation indicating that an increase in interfacial tension would result in decreasing the width of the ambivalent region.

A study by McClarey and Mansoori (1978) shows that temperature, density difference and viscosity difference between the mixed phases are the most important factors to be effective on phase inversion. In addition, at low mixing speeds the wettability of phases with the mixing tank surface could also determine the dispersed phase.

Arashmid and Jeffreys (1980) quantified the parameters controlling phase inversion. They combined the correlations of collision frequency and coalescence frequency with the models relating drop size and dispersed phase hold-up to the mixing speed to predict the ambivalent region and phase inversion compositions.

2.2.3 Drop Size

In an agitated vessel it is expected that the droplets continually coalesce and redisperse, so that a drop size distribution is produced. The mean size represents a dynamic equilibrium between the break-up and coalescence phenomena, with the characteristics of break-up predominating in dilute dispersions and those of coalescence in concentrated. Furthermore, it is known that the velocity of the liquid in an agitated vessel varies from place to place, being greatest in the immediate vicinity of the impeller blades (Sachs and Rushton 1954, Norwood and Metzner, 1960). Therefore, one may expect a variation in the vessel. These variations in size have been observed (Calderbank, 1958, Sprow, 1967b, Mlynek and Resnick, 1972, Weinstein and Treybal, 1973) and coalescence with redispersion has been proved (Madden and Damerell,1962, Coulaloglou and Tavlarides, 1977, Verhoff et al., 1977, Ross et al., 1978).

Based on the theory of local isotropy (Kolmogoroff, 1941a,b) expressions have been derived (Shinnar, 1961, Sprow, 1967a) for the maximum drop diameter than can be obtained in locally isotropic regions in a baffled vessel. Two mechanisms are apparent: one in which inertial effects predominate in the break-up of a drop, and another in which viscous forces cause break-up. The resulting equations are :

$$\phi_{max} = C_{2.2}\, \sigma^{3/5}\, \rho_c^{-3/5}\, N^{-6/5}\, D^{-4/5} \qquad (2.15)$$

for break-up through inertial effects, and

$$\phi_{max} = C_{2.3}\, \sigma\, \nu_c^{1/2}\, \mu_c^{-1}\, N^{-3/2}\, D^{-1}\, f(\mu_d/\mu_c) \qquad (2.16)$$

for break-up due to viscous shear.

It is usually believed (Shinnar, 1961) that equations (2.15) and (2.16) should apply to droplets larger and smaller than the Kolmogoroff length, respectively. The Kolmogoroff length η is defined as :

$$\eta = (\nu_c^3/e)^{1/4} \qquad (2.17)$$

where e is the rate of energy dissipation per unit mass.

Shinnar and Church (1960), Shinnar (1961) and Sprow (1967b) derived an expression for the minimum stable droplet diameter for a locally isotropic flow field and in the region of inertial effects as :

$$\phi_{min} = C_{2.4} F^{3/8} \rho_c^{-3/8} N^{-3/4} D^{-1/2} \qquad (2.18)$$

where F is a force parameter representing the force of interaction between two particles.

For the region of viscous shear, Sprow (1967b) suggested the following equation

$$\phi_{min} = C_{2.5} F^{1/2} \nu_c^{1/4} \mu_c^{-1/2} N^{-3/4} D^{-1/2} \qquad (2.19)$$

It is clear that the diameters defined in equations (2.15), (2.16), (2.18) and (2.19) are in reality statistical averages; in the case of (2.15) and (2.16) of the drop size at which break-up most probably occurs, and in the case of (2.18) and (2.19) of the drop size above which prevention of coalescence becomes effective.

The parameter of interest is the Sauter mean drop diameter, ϕ_{32} which is related to the surface area per unit volume, S, and hold-up of the dispersed phase, ε, by the equation :

$$\phi_{32} = \frac{6\varepsilon}{S} \qquad (2.20)$$

A summary of the various correlations currently available in the literature for Sauter mean diameters in agitated vessels is given in Table 2.3. Care should be taken in any comparisons because of the variety of operating conditions, range of

Table 2.3 Correlations Predicting Drop Sizes in Agitated Vessels

Correlation	Physical Properties ρ_d kg/m^3	μ_d mPa s	σ mN/m	Batch/ Continuous	Operating Conditions T m	D m	N 1/s	ϵ	Experimental Techniques and Comments
Vermeulen et al. (1955) :									
$\frac{\phi_{32}}{D} = 0.084\{\frac{(0.4\rho_c+0.6\rho_d)N^2D^3}{\sigma}\}^{-0.6} f(\epsilon)$	693.0- 1595.0	0.378- 184.0	3.6- 55.1	Batch	0.254, 0.508	0.172, 0.33	1.58- 6.67	0.10- 0.40	Light Transmittance
Calderbank (1958) :									
$\frac{\phi_{32}}{D} = 0.06We_T^{-0.6}(1+3.75\epsilon)$ (4 blade paddle)	870.0- 1595.0	0.590- 0.980	35.0- 40.0	Batch	0.178, 0.381	0.058- 0.254	-	0.0- 0.20	Light Transmittance
$\frac{\phi_{32}}{D} = 0.06We_T^{-0.6}(1+9\epsilon)$ (6 blade paddle)									
Kafarov and Babanov (1959) :									
$\frac{\phi_{32}}{D} = C_{2.6}(\frac{\rho_m N^2D^3}{\sigma})^{-0.5}(\frac{\rho_m ND^2}{\mu_m})^{-0.1}\epsilon^{0.16}$	779.9- 1000.6	0.59- 192.3	22.6- 56.9	Batch	0.2, 0.4	0.067, 0.133	1.67- 16.67	0.05- 0.35	Sedimentometery, Photography
Pavlushenko and Yanishevskii (1959) :									
$\frac{\phi_{32}}{D} = 0.028We_T^{-0.56}(\frac{\rho_c ND^2}{\mu_c})^{0.12}(\frac{\Delta\rho}{\rho_c})^{-0.25} \cdot (\frac{\mu_c}{\mu_d})^{-0.27}(\frac{T}{D})^{1.21}\epsilon^{0.68}$	704.4- 1020.2	0.630- 248.2	1.6- 48.6	Batch	0.2, 0.3	0.05- 0.15	-	0.075- 0.40	Photography
Rodriguez et al. (1961) :									
$\frac{\phi_{32}}{D} = C_{2.7}We_T^{-0.6}(\frac{T}{D})^{1.2}\epsilon$	834.0	-	13.9	Batch	0.152- 0.391	0.05- 0.152	2.5- 18.33	0.40	Light Transmittance
Shinnar and Church (1960) and Sprow (1967b) :									
$\frac{\phi_{32}}{D} = C_{2.8}We_T^{-0.375}(\frac{F}{\sigma D})^{0.375}$	800.0	0.59	9.3	Batch	0.222	0.063	8.33- 33.33	0.25	Coulter-Counter, Strongly Coalescing Systems (Sprow, 1967b)
Sprow (1967a) :									
$\frac{\phi_{32}}{D} = 0.0524We_T^{-0.6}$	692.0	0.51	41.8	Batch	0.222	0.032- 0.102	4.17- 33.33	0.005- 0.015	Coulter-Counter

Table 2.3 (Continued)

Correlation	Physical Properties				Operating Conditions				Experimental Techniques and Comments
	ρ_d kg/m^3	μ_d mPa s	σ mN/m	Batch/ Continuous	T m	D m	N 1/s	ε	
Bouyatiotis and Thornton (1967) :									
$\frac{\phi_{32}}{D} = \phi_{32}^0 + 1.18\left(\frac{\sigma^2}{\mu_c^2 g}\right)\left(\frac{\Delta\rho\sigma^3}{\mu_c^4 g}\right)^{-0.62}\left(\frac{\Delta\rho}{\rho_c}\right)^{0.05}\varepsilon$	691.0- 905.0	0.486- 0.748	8.5- 40.0	Batch, Continuous	0.178	0.069	6.67- 16.67	0.2- 0.5	Photography
Chen and Middleman (1967) :									
$\frac{\phi_{32}}{D} = 0.053 We_T^{-0.6}$	703.0- 1101.0	0.520- 25.8	4.75- 48.3	Batch	0.102- 0.457	0.051- 0.152	1.33- 16.67	0.001- 0.005	Photography
Brown and Pitt (1970) :									
$\frac{\phi_{32}}{D} = 0.051 We_T^{-0.6}\ (1+3.14\varepsilon)$	783.0- 838.0	0.59- 3.30	1.9- 5.0	Batch	0.30	0.10	4.17- 7.50	0.05- 0.30	Light Transmittance
van Heuven (1969) and van Heuven and Beek (1971)									
$\frac{\phi_{32}}{D} = 0.047 We_T^{-0.6}\ (1+2.5\varepsilon)$	660.0- 910.0	-	8.5- 49.5	Batch	0.125- 1.20	0.0375- 0.40	2.8- 10.2	0.004- 0.35	Encapsulation, Photography of Stablized Emulsion
Mlynek and Resnick (1972) :									
$\frac{\phi_{32}}{D} = 0.058 We_T^{-0.6}\ (1+5.4\varepsilon)$	1055.0	-	41.0	Batch	0.29	0.09, 0.10	2.5- 8.33	0.025- 0.34	Encapsulation
Moser et al. (1975) :									
$\frac{\phi_{32}}{D} = 0.024 We_T^{-0.6}\ (1+3.4\varepsilon)$	-	-	-	Batch	-	-	5.0- 10.0	0.05- 0.20	Photography of Stablized Emulsion
Coulaloglou and Tavlarides (1976) :									
$\frac{\phi_{32}}{D} = 0.081 We_T^{-0.6}\ (1+4.47\varepsilon)$	972.0	1.30	43.0	Continuous	0.244	0.10	3.17- 5.17	0.025- 0.15	Photomicrography
Gnanasundaram et al. (1979) :									
$\frac{\phi_{32}}{D} = 0.052 We_T^{-0.6} \exp(4\varepsilon)$ for $We_T < 10^4$ $\frac{\phi_{32}}{D} = 0.39 We_T^{-0.6}$ for $We_T > 10^4$	-	-	1.5- 45.0	Batch, Continuous	0.102- 0.86	0.044- 0.28	1.67- 35.0	0.01- 0.50	Photography, Chemical Reaction

Table 2.3 (Continued)

Correlation	Physical Properties			Batch/ Continuous	Operating Conditions				Experimental Techniques and Comments
	ρ_d kg/m3	μ_d mPa s	σ mN/m		T m	D m	N 1/s	ε	
Skelland and Lee (1981) : $\frac{\phi_{32}}{D} = 6.713\times10^{-4} \left(\frac{D}{T}\right)^{-1.034} \left(\frac{\rho_c N D^2}{\mu_c}\right)^{-0.558}$ $\cdot\{\mu_c/(\rho_c D\,\sigma)^{1/2}\}^{-1.025}\ \varepsilon^{0.188}$	873.0- 1041.0	0.46- 1.9	6.0- 39.0	Batch	0.210, 0.246	0.078, 0.106	3.0- 8.0	0.03- 0.09	Photography, Mass Transfer Conditions

physical properties and effects of trace amount of impurities.

Most of the correlations in Table 2.3 may be put in the following general form in terms of tank Weber number, $We_T = (\rho_c N^2 D^3/\sigma)$, and hold-up, ε :

$$\frac{\phi_{32}}{D} = C_{2.9} We_T^{-0.6} f(\varepsilon) \qquad (2.21)$$

The hold-up function $f(\varepsilon)$ can be expressed by the linear relation :

$$f(\varepsilon) = 1 + C_{2.10}\varepsilon \qquad (2.22)$$

There does not seem to be any general agreement on the values of $C_{2.10}$, the reported range varying between 2.5 and 9.

Doulah (1975) argued that because the dispersion viscosity depends on hold-up and because turbulent scales are affected, drop sizes in concentrated dispersions should depend on the dispersion viscosity. He shows that the hold-up function defined by equation (2.22) is in fact due to a reduction of turbulence intensities in the presence of the dispersed phase.

Delichatsios and Probstein (1976) suggested that the increase in drop size with dispersed phase volume fraction cannot be attributed entirely to turbulence damping caused by the dispersed phase. Their analysis shows that increased drop size with higher fractional hold-up can be accounted for by allowing for coalescence. These authors have given a semi-empirical equation for the hold-up function :

$$f(\varepsilon) = \{-\frac{1}{4.5}\ell n(0.011 + C_{2.11}\varepsilon)\}^{-3/5} \qquad (2.23)$$

The constant $C_{2.11}$, which depends on the ratio of coalescence to break-up coefficients, must be determined empirically since it is expected to vary with the purity of the dispersion.

2.3 Motion of Liquid Drops

The study of motion of a drop swarm through a mobile continuous phase medium is an important aspect of liquid/liquid extraction since velocities of the drop phase determine the hold-up of the dispersed phase in an extraction column. However, the hydrodynamic aspects are so complex that there is a serious lack of quantitative information, and on the other hand, there are many assumptions in the mathematical models used to describe the situation. The drag force acting on a liquid drop will not, in general, be the same as that acting on a rigid particle because the circulation inside the drop reduces the velocity gradient at the fluid/liquid interface, thereby reducing the drag force. In addition, the drops deform and oscillate unless they are very small, so that the interfacial tension forces predominate. The drag force acting on a drop in a drop swarm is further complicated by the complex motion of the continuous phase between the drops.

2.3.1 Terminal Velocities of Single Drops

Very small drops behave like rigid spheres and their velocity can be described by Stokes' law (creeping flow). The total drag force, F_D, can be obtained analytically by solving the Navier-Stokes equations of motion, neglecting the inertial term and assuming, as boundary conditions, zero velocity on the drop surface. The simple Stokes' law of resistance thus obtained is :

$$F_D = 3\pi\mu_c\phi U \tag{2.24a}$$

$$C_D = \frac{24\mu_c}{\rho_c U\phi} = \frac{24}{Re} \tag{2.24b}$$

$$U = \frac{\phi^2 \Delta\rho g}{18\mu_c} \tag{2.24c}$$

which holds at Re of 0.2 or less. The total drag force is composed of both skin friction and form drag.

Utilizing the ideal internal circulation model, Hadamard (1911) and Rybczinski (1911) arrived at a Stokes' law correction factor as given below :

$$F_D = 3\pi\mu_c\phi U \left(\frac{3\mu_d + 2\mu_c}{3\mu_d + 3\mu_c}\right) \qquad (2.25a)$$

and the terminal velocity of the mobile drop is given by :

$$U = \frac{\phi^2\Delta\rho g}{18\mu_c} \left(\frac{3\mu_d + 3\mu_c}{3\mu_d + 2\mu_c}\right) \qquad (2.25b)$$

Surface tension forces act in a direction tangent to the interface. Boussinesq (1913) assumed that for a surface undergoing "dilation" there must be another force acting normal to the interface. He gave a Stokes' law correction factor as :

$$F_D = 3\pi\mu_c\phi U \left\{\frac{\zeta + \frac{\phi}{2}(3\mu_d + 2\mu_c)}{\zeta + \frac{\phi}{2}(3\mu_d + 3\mu_c)}\right\} \qquad (2.26a)$$

and hence

$$U = \frac{\phi^2\Delta\rho g}{18\mu_c} \left\{\frac{\zeta + \frac{\phi}{2}(3\mu_d + 3\mu_c)}{\zeta + \frac{\phi}{2}(3\mu_d + 2\mu_c)}\right\} \qquad (2.26b)$$

in which ζ is the dynamic increment to the normal surface tension,which he called "surface viscosity", determinable from experimental data.

The derivations of Hadamard (1911), Rybczinski (1911) and Boussinesq (1913) hold for laminar flow of both drop and continuous fluids. The upper limit of applicability of these equations is thought of as Re $\simeq$ 1.

In the derivation of the preceding equations inertial forces were neglected but most practical situations involve both viscous and inertial forces. However, the Navier-Stokes equations can not then be solved and empirical formulæ are required.

For Re $>$ 10, the terminal velocities of single drops as a function of drop size and physical properties of liquid/liquid systems have been investigated by many authors (Hu and Kintner, 1955, Keith and Hixson, 1955, Licht and Narasimhamurthy, 1955, Klee and Treybal, 1956, Johnson and Braida, 1957, Strom and

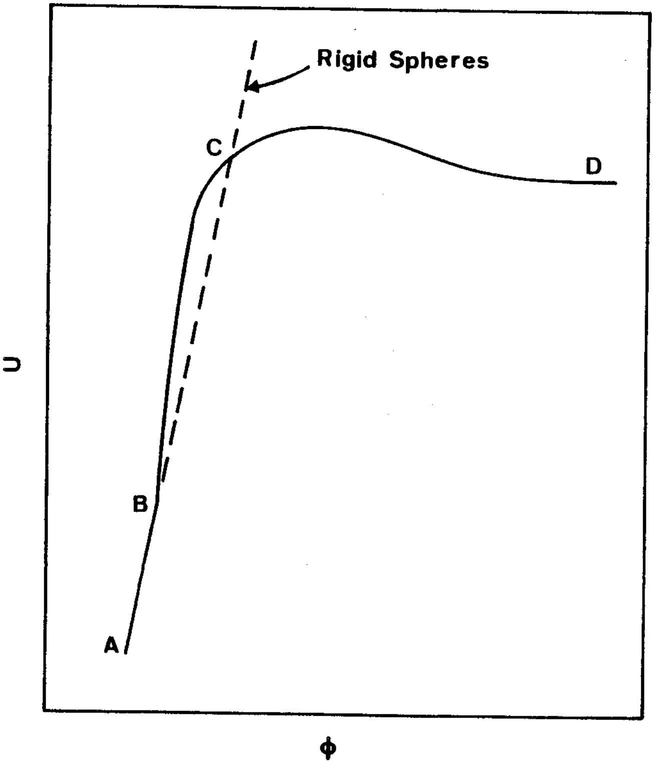


Figure 2.2 Typical Terminal Velocity Curve

Kintner,1958, Krishna et al., 1959, Warshay et al.,1959, Harmathy, 1960 and Elzinga and Banchero, 1961). A typical plot of terminal velocity versus equivalent drop diameter for low viscosity continuous liquids is shown in Figure 2.2. Small drops in region AB will be spherical in shape, will not circulate internally and their terminal velocity will generally be that of a rigid sphere of equal size and density moving in the same continuous liquid. As the drop diameter is increasedthe curve BC deviates from the rigid sphere line owing to the gradual distortion of the drop from the spherical to an ellipsoidal shape with the minor axis oriented along the direction of movement.

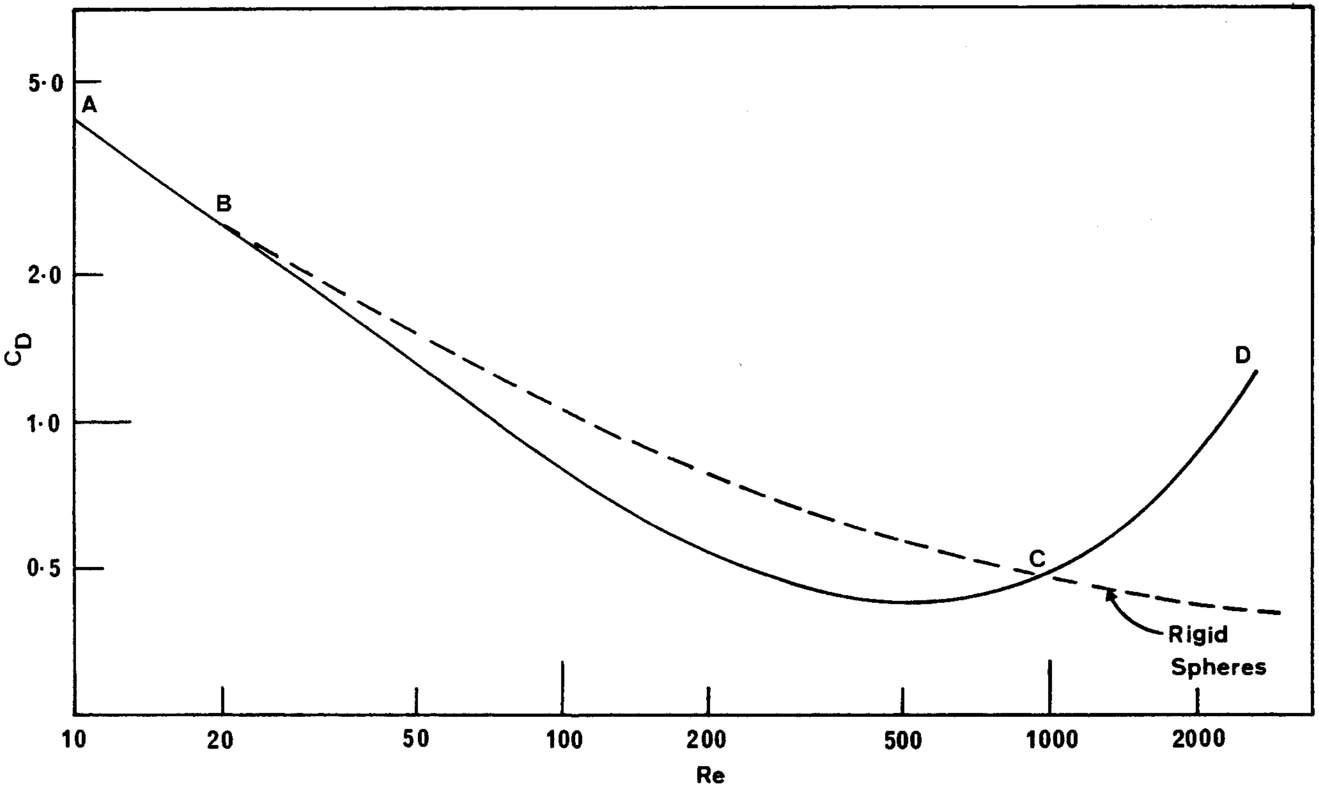


Figure 2.3 Typical Variation of Drag Coefficient with Reynolds Number for Liquid Drops; the Actual Relationship for Rigid Spheres is Indicated by Dashed Line

As the drop size is increased further the terminal velocity passes through a maximum, or peak, velocity. After this peak point, a further increase in drop diameter does not result in any appreciable change in terminal velocity which attains constancy, independent of drop size, till a maximum possible drop size is reached. This condition is shown by curve CD. Beyond this, drops can not exist as single entities but will break up into two or more smaller ones.

A typical drag curve will appear as in Figure 2.3. The equivalent drop diameter has been used in both C_D and Re. Small drops at low Reynolds numbers take the path of rigid spheres along the curve AB. At a Reynolds number of about 1000 there is an abrupt increase in drag coefficient, after which drop break-up occurs. The region of abrupt change is represented by curve CD, The break in drag coefficient corresponds to the oscillation threshold and this corresponds to the maximum terminal velocity (Garner and Skelland, 1955, Hu and Kintner, 1955, Klee and Treybal, 1956).

Many empirical correlations for the terminal velocities of liquid drops are available in the literature (Hu and Kintner, 1955, Licht and Narasimhamurthy, 1955, Klee and Treybal, 1956, Johnson and Braida, 1957, Krishna et al., 1959, Harmathy, 1960). The most frequently used equations of Hu and Kintner can be re-written as :

$$\frac{\rho_c U\phi}{\mu_c} = P^{0.15}\left\{0.798\left(\frac{4\Delta\rho g\phi^2 P^{0.15}}{3\sigma}\right)^{0.784} - 0.75\right\} \qquad (2.27a)$$

for $2 < \dfrac{4\Delta\rho g\phi^2 P^{0.15}}{3\sigma} \leq 70$

and

$$\frac{\rho_c U\phi}{\mu_c} = P^{0.15}\left\{3.701\left(\frac{4\Delta\rho g\phi^2 P^{0.15}}{3\sigma}\right)^{0.422} - 0.75\right\} \qquad (2.27b)$$

for $\dfrac{4\Delta\rho g\phi^2 P^{0.15}}{3\sigma} > 70$

where $P = (\rho_c^2\sigma^3)/(g\mu_c^4\Delta\rho)$. These equations were reported to give errors below 10 percent in the terminal velocity.

Klee and Treybal (1956) also arrived at two equations, one for the region below the peak terminal velocity and one for that above the peak. Their equations, in SI units, are as follows:

$$U = 3.04\ \rho_c^{-0.45}\ \Delta\rho^{0.58}\ \mu_c^{-0.11}\ \phi^{0.70} \qquad (2.28a)$$

and

$$U = 4.96\ \rho_c^{-0.55}\ \Delta\rho^{0.28}\ \mu_c^{0.10}\ \sigma^{0.18} \qquad (2.28b)$$

The transition diameter ϕ_T, is given by the solution of these two equations as :

$$\phi_T = 1.77\ \rho_c^{-0.14}\Delta\rho^{-0.43}\ \mu_c^{0.30}\ \sigma^{0.18} \qquad (2.28c)$$

These authors warn that their equations are simply good approximations and describe their data and those of other authors fairly accurately. The continuous liquid in all systems used was one of low viscosity.

2.3.2 Dispersed Phase Hold-up and Slip Velocity in Spray Extraction Columns

The extensive study of Mertes and Rhodes (1955) and later the work of Lapidus and Elgin (1957) have shown that the concept of slip velocity can be used to compare and correlate dispersed phase hold-up data in solvent extraction columns. The slip velocity V_s, of a droplet relative to the continuous phase in a multidrop dispersion is related to the apparent velocities of the continuous and dispersed phases, V_c and V_d by :

$$V_s = \frac{V_c}{1-\varepsilon} + \frac{V_d}{\varepsilon} \qquad (2.29)$$

The slip velocity is normally correlated by using different parameters (drop size, hold-up and physical properties of the phases) and the dispersed phase hold-up is computed numerically.

Ergun (1952) developed an equation for the pressure drop in packed beds which was extended by Andersson (1961) for ideally fluidized beds consisting of solid spheres of uniform size by including a tortuosity factor, q', and a cross-section factor, w, both of which are functions of void fraction. The Andersson equation can be re-written for countercurrent flow of two immiscible liquids, when one of the liquids is dispersed as droplets in the other, as :

$$\frac{\Delta p}{L} = 36wq'^2 \left(\frac{\varepsilon}{1-\varepsilon}\right)^2 \frac{\mu_c V_s}{\phi_{32}^2} + 6C_I q'^3 \left(\frac{\varepsilon}{1-\varepsilon}\right) \frac{\rho_c V_s^2}{\phi_{32}} \tag{2.30}$$

This equation is related to the hold-up of the dispersed phase by the static pressure drop formula:

$$\frac{\Delta p}{L} = g\Delta\rho\varepsilon \tag{2.31}$$

The inertial drag coefficient, C_I, which is a measure of the deviation from Stokes' law, is given by :

$$C_I = \frac{1}{8}\left(C_D - \frac{24}{Re}\right) \tag{2.32}$$

and it can be calculated by using the velocity, U, of a single drop in an infinite medium using equations (2.27a,b) of Hu and Kintner or equations (2.28a-c) of Klee and Treybal.

Based on experimental data of spray columns, Pilhofer (1974) gave empirical expressions for the correction factors wq'^2 and q'^3 which are slightly different from those reported by Andersson for fluidized beds :

$$wq'^2 = \frac{1-\varepsilon}{2\varepsilon} \exp\left(\frac{\varepsilon}{0.4-0.244\varepsilon}\right) \quad \text{for } 0.06 < \varepsilon < 0.55 \tag{2.33a}$$

$$wq'^2 = 2.2\,\frac{1-\varepsilon}{\varepsilon} \exp\left(\frac{0.44\varepsilon}{1-0.61\varepsilon}\right) \quad \text{for } 0.55 < \varepsilon < 0.74 \tag{2.33b}$$

and

$$q'^3 = 5\left(\frac{\varepsilon}{1-\varepsilon}\right)^{0.45} \left\{1 - 0.31\left(\frac{\mu_c}{\mu_d}\right)^{0.39}\right\} \tag{2.33c}$$

Combining equations (2.30) and (2.31) and re-writing, one obtains:

$$Ar \quad = \quad 36wq'^2 \frac{\varepsilon}{(1-\varepsilon)^2} Re_{\varepsilon,0} \quad + \quad \frac{6C_I q'^3}{(1-\varepsilon)} Re^2_{\varepsilon,0} \qquad (2.34)$$

where $Ar = g\Delta\rho\phi^3_{32}\, \rho_c/\mu^2_c$ and $Re_{\varepsilon,0} = \rho_c V_s \phi_{32}/\mu_c$. Solving equation (2.34) for $Re_{\varepsilon,0}$, the following expression is obtained :

$$\frac{\rho_c V_s \phi_{32}}{\mu_c} = \frac{3wq'^2}{(1-\varepsilon)q'^3 C_I} \left[\left\{ \left(\frac{C_I q'^3 Ar (1-\varepsilon)^3}{54(wq'^2\varepsilon)^2} \right) + 1 \right\}^{1/2} - 1 \right] \qquad (2.35)$$

Pilhofer used equations (2.27a,b) to calculate C_I and found that the slip velocities calculated from equation (2.35) were too low when $(4\Delta\rho g\phi^2 P^{0.15})/(3\sigma) > 70$. For this reason he modified equation (2.32) to :

$$C_I = \frac{1}{8}\left(C_D - \frac{24}{Re}\right) \left\{1 - \varepsilon^{1.29}\left(\frac{Ar-Ar_G}{Ar_G}\right)^{-1.74}\right\} \qquad (2.36)$$

where Ar_G is the Archimedes number at $(4\Delta\rho g\phi^2 P^{0.15})/(3\sigma) = 70$, calculated from

$$Ar_G = 371.9P^{0.275} \qquad (2.37)$$

Modified values of C_I calculated from equation (2.36) are sometimes negative (Kumar et al., 1980). Better agreement between experimental and calculated slip velocities can be obtained if the following equation (Pilhofer, 1979) is used for the region $(4\Delta\rho g\phi^2 P^{0.15})/(3\sigma) > 70$:

$$C_I = \frac{1}{8}\left(C_D - \frac{24}{Re}\right) \left\{1 - \varepsilon^{1.19}\left(\frac{Ar - Ar_G}{Ar_G}\right)^{0.47}\right\} \qquad (2.38)$$

In such a situation equation (2.33c) defining q'^3 should be retained (whereas the definition $q'^3 = 5\{\varepsilon/(1-\varepsilon)\}^{0.45}$ should be used in conjunction with equation (2.36)).

Zenz (1957) suggested that the necessary trial-and-error procedure for estimating terminal velocity in terms of particle diameter can be avoided if $(Re/C_D)^{1/3}$ is plotted against $(Re^2 C_D)^{1/3}$ which is, in effect, a plot of terminal velocity versus diameter of the particle, the other quantities involved being simply the physical properties of the system. In a similar manner, Barnea and Mizrahi (1975e) correlated the data on spray columns using extended definitions of drag coefficients and Reynolds number, taking into account momentum transfer, wall and hydrostatic effects, as given below :

$$C_{D\varepsilon,1} = \frac{4\Delta\rho g\phi_{32}}{3\rho_c V_s^2} \cdot \frac{(1-\varepsilon)}{(1+\varepsilon^{1/3})} \tag{2.39}$$

and

$$Re_{\varepsilon,1} = \frac{\rho_c V_s \phi_{32}}{\mu_\varepsilon} \tag{2.40}$$

where μ_ε is the effective viscosity of the dispersion. An expression for calculating μ_ε was also provided :

$$\mu_\varepsilon = \mu_c \, B\left(\frac{\frac{2}{3}B + \frac{\mu_d^*}{\mu_c}}{B + \frac{\mu_d^*}{\mu_c}}\right) \tag{2.41a}$$

where

$$B = \exp\left\{\frac{5\,\varepsilon}{3(1-\varepsilon)}\left(\frac{\mu_c + 2.5\mu_d}{2.5\mu_c + 2.5\mu_d}\right)\right\} \tag{2.41b}$$

and μ^*_d is the effective viscosity of the dispersed phase. However, due to difficulties in estimating μ_d^* these authors used μ_d instead of μ_d^* for the calculation of μ_ε. They plotted $(Re_{\varepsilon,1}/C_{D\varepsilon,1})^{1/3}$ versus $(Re_{\varepsilon,1}^2 C_{D\varepsilon,1})^{1/3}$ for 88 data points on 12 liquid/liquid systems and showed that the C_D-Re correlation for a single solid sphere in an infinite fluid medium fitted the data points satisfactorily.

Ishii and Zuber (1979) gave drag coefficient and slip velocity correlations for the dispersed two-phase flow of bubbles, drops and solid particles. They defined the drag coefficient for multi-particle systems as :

$$C_{D\varepsilon,2} = \frac{4\Delta\rho g\phi(1-\varepsilon)}{3\rho_c V_s^2} \tag{2.42}$$

whereas the Reynolds number was defined in the same manner as by Barnea and Mizrahi (equation (2.40)), but a different expression was given for the effective viscosity of multi-particle systems. A set of equations relating the drag coefficient to the Reynolds number with their limits of applicability has been provided by these authors.

Thornton (1956) suggested another relationship to correlate the hold-up in spray columns :

$$V_o(1-\varepsilon) = \frac{V_c}{1-\varepsilon} + \frac{V_d}{\varepsilon} \qquad (2.43)$$

where V_o is termed as the characteristic velocity of the drop swarm and may be identified with the actual terminal velocity of a single drop when V_c is zero and V_d tends to zero. Equation (2.43) suggests that for a particular liquid/liquid system and distributor geometry a plot of $(V_d + V_c \frac{\varepsilon}{1-\varepsilon})$ versus $\varepsilon(1-\varepsilon)$ should be a straight line passing through the origin with V_o as its slope. However, for each of the 4 liquid/liquid systems and 7 different distributors used, Vedaiyan (1969) found that such plots were curvilinear and attributed the deviation from constancy of V_o to variation of drop size with the dispersed phase throughput. He also gave a correlation for V_o in terms of nozzle diameter, nozzle velocity and physical properties of the liquid phases as :

$$V_o/\left(\frac{\sigma\Delta\rho g}{\rho_c^2}\right)^{1/4} = 1.088\left(\frac{v^2}{2gd}\right)^{-0.082} \qquad (2.44)$$

Continuous phase viscosity was found to have no effect on V_o and the average error for about 300 data points was reported to be 10.3%.

2.3.3 Dispersed Phase Hold-up in Pulsed Sieve-Plate Extraction Columns

Although spray columns are simple to construct, are inexpensive and have high flow capacity, they have poor efficiencies. This is largely due to the high degree of backmixing of the continuous phase taking place in the column. It is normally difficult to obtain an equivalent of more than a few theoretical stages in a single spray column installation. The degree of dispersion and hence the mass transfer rates can be considerably enhanced by the introduction of some form of mechanical agitation. In a pulsed sieve-plate liquid/liquid extraction column an axial pulsing motion is superimposed on the countercurrent flow of the liquid phases. The agitation is produced as the phases flow through small holes in the horizontal plates regularly spaced along the column axis.

The existence of different flow regimes in pulsed sieve-plate columns has been observed by many authors (Sege and Woodfield, 1954, Sehmel, 1961, Sehmel and Babb, 1963, Sato et al., 1963, Bell, 1964, Bell and Babb, 1969). These regions are ill-defined but may be classified in terms of phase throughputs and frequencies. The mixer-settler regime occurs at low throughputs and frequencies; the light phase initially resting under the sieve plate is forced through the holes during the upward movement of the pulse, the heavy phase descending during the downward movement of the pulse. The hold-up is high at low frequencies and decreases as the frequency increases until a minimum is reached, corresponding to the beginning of the dispersion regime. In the dispersion regime the hold-up increases slowly with increasing frequency. Emulsion-type operation, occurring at higher throughputs and frequencies, and characterized by uniform dispersion of one phase in the other, provides good conditions for mass transfer due to the intimate contact of the phases and high degree of agitation. A further increase in throughput or frequency leads to unstable operation due to irregular coalescence and localized phase inversions in different sections of the column and is quickly followed by flooding.

The correlations discussed in this section and in Chapter 4 are based on the above definitions of the regions involved.

Hold-up is an essential parameter in the design of extraction equipment; a number of authors have given empirical correlations for the prediction of hold-up in pulsed sieve-plate extraction columns, as summarized in Table 2.4.

Thornton (1957) correlated the hold-up of the dispersed phase on the basis of characteristic velocity and is only valid for the emulsion region of operation. Miyauchi and Oya (1965) defined the mean rate of energy dissipation per unit mass of mixed phases, e, (having dimensions of length squared divided by time cubed), as :

$$e = C_{2.18} \frac{(Af)^3}{\lambda \ell} \qquad (2.45)$$

where A is the pulsation stroke (twice the amplitude), f the frequency of oscillation, ℓ the plate spacing and λ a function of the plate free area, κ, given by :

$$\lambda = \frac{\kappa^2}{(1-\kappa)(1-\kappa^2)} \qquad (2.46a)$$

The dimensionless proportionality constant $C_{2.18}$ is defined by

$$C_{2.18} = \frac{5\pi^2}{6\sqrt{2}} \cdot \frac{1 + \ell/L}{c_o^2} \qquad (2.46b)$$

in which L is the column length and c_o the discharge doefficient for the flow through holes in the sieve plate. When $\ell \ll L$ and $c_o \simeq 0.61$ the value of $C_{2.18}$ is 15.6.

Miyauchi and Oya found that it was necessary to include the dispersed phase velocity to correlate the hold-up data and postulated that the boundary between dispersion and emulsion regions occurred when ξ, defined by $(\mu_d^2/\sigma\Delta\rho)^{1/4}\cdot Af/(\lambda\ell)^{1/3}$, was equal to 0.0031 $m^{11/12}/s$. In view of the peculiar units it is not clear why the authors chose to modify e (defined by equation (2.45) in this way.

The parabolic form of the correlation of Bell and Babb (1969) enables the hold-up to be calculated in all three regimes of

Table 2.4 Correlations Predicting Hold-up in Pulsed Sieve-Plate Extraction Columns

Correlation (cgs units)	Remarks
Sato et al. (1963) :	
$\varepsilon = 0.52\left(\frac{Af}{V_d}\right)^{-0.70} \left(1+\frac{V_d}{V_c}\right)^{-0.70} \ell^{-1.2} d_o^{-0.26}$	Mixer-Settler Region
for $0 < Af \leq 1.3\ V_d^{0.22}\ \ell^{-0.32}\ d_o^{-0.37}$	
$\varepsilon = 0.42(Af)\ V_d^{0.33} \left(1+\frac{V_d}{V_c}\right)^{-0.70} \ell^{-0.68} d_o^{0.37}$	Dispersion Region
for $1.3\ V_d^{0.22}\ \ell^{-0.32}\ d_o^{-0.37} \leq Af \leq 0.8\ V_d^{0.22}\ \ell^{0.35}\ d_o^{-0.37}$	
$\varepsilon = 0.54(Af)^{2.4} \left(1+\frac{V_d}{V_c}\right)^{-0.70} \ell^{-1.2} d_o^{0.89}$	Emulsion Region
for $Af \geq 0.8\ V_d^{0.22}\ \ell^{0.35}\ d_o^{-0.37}$	System: Methyl isobutyl ketone(d)/acetic acid/ water(c)
Miyauchi and Oya (1965) :	
$\varepsilon = 0.66\ V_d^{2/3}\ \xi^{0.84}$; $\xi < 0.21$	Dispersion Region
$\varepsilon = 6.32\ V_d^{2/3}\ \xi^{2.4}$; $\xi > 0.21$	Emulsion Region
where $\xi = \frac{Af}{(\lambda\ell)^{1/3}} \cdot \left(\frac{\mu_d^2}{\sigma\Delta\rho}\right)^{1/4}$ and $\lambda = \frac{\kappa^2}{(1-\kappa)(1-\kappa^2)}$	

Table 2.4 (Continued)

Correlation (cgs units)	Remarks
Angelino et al. (1967) :	
$\varepsilon \approx C_{2.12} \left(\frac{Af\ \mu_c}{\sigma}\right)^{1.4}$	
Bell and Babb (1969) :	
$\varepsilon = V_d\{C_{2.13} + (C_{2.14} + C_{2.15}\ V_c)(Af - C_{2.16})^2\}$	$C_{2.13}$, $C_{2.16}$ - constants dependent on physical properties $C_{2.14}$, $C_{2.15}$ - constants dependent on column geometry
Mishra and Dutt (1969) :	
$\varepsilon = C_{2.17} \left\{ \frac{(Af)^3}{\lambda \ell} \right\}^{0.27} V_d^{0.89}\ d_o^{-0.924}$	$C_{2.17}$ – constant dependent on physical properties of system λ - as defined by Miyauchi and Oya (1965)
Arthayukti (1975) :	
$\varepsilon = 0.38\ V_d^{2/3}\ \xi^{0.75}$; $Af < 4.57$ cm/s	ξ - as defined by Miyauchi and Oya (1965)
$\varepsilon = 3.46\ V_d^{2/3}\ \xi^{2.62}$; $Af > 4.57$ cm/s	System: Carbontetrachloride(d)/ water(c)

Table 2.4 (Continued)

Correlation (cgs units)		Remarks
Khemangkorn et al. (1979) :		
$\varepsilon = 3.04\mathrm{x}10^{-2}\ V_d\ (Af^{1.24})^{1.26}$	; $Af^{1.24} < 5.5\ \mathrm{cm/s}^{1.24}$	direction c → d
$\varepsilon = 5.40\mathrm{x}10^{-4}\ V_d^{2/3}\ (Af^{1.24})^{2.91}$	; $Af^{1.24} \geq 5.5\ \mathrm{cm/s}^{1.24}$	
$\varepsilon = 2.66\mathrm{x}10^{-2}\ V_d\ (Af^{1.24})^{1.38}$	; $Af^{1.24} < 5.2\ \mathrm{cm/s}^{1.24}$	direction d → c
$\varepsilon = 2.30\mathrm{x}10^{-4}\ V_d^{2/3}\ (Af^{1.24})^{3.45}$	; $Af^{1.24} \geq 5.2\ \mathrm{cm/s}^{1.24}$	
		System: Carbontetrachloride(d)/ iodine/water(c)

a pulsed sieve-plate column but requires the empirical determination of the constants $C_{2.13}$ and $C_{2.16}$ dependent on the physical properties of the liquid/liquid system and $C_{2.14}$ and $C_{2.15}$ dependent on the column geometry.

Although in Mishra and Dutt's (1969) work the hole diameter d_o did not vary greatly (4.8 to 6.4 mm), a strong dependence of hold-up on this dimension in the dispersion region of operation was reported by these authors.

3. COALESCENCE OF SINGLE DROPS AND DROPLET DISPERSIONS

In liquid/liquid extraction processes intimate contacting of the solvent phases to achieve good mass transfer is followed by separation of the phases to recover solvents and solute. To enhance mass transfer the interfacial area should be increased by breaking droplets into a fine dispersion, but easy separation requires a dispersion of large drops. Since both steps are important in an extraction process, this poses a difficult problem in the design of the apparatus.

The rate of separation depends on the drop size, drop size distribution, density difference and viscosities of the liquids, interfacial tension and hold-up of the dispersed phase. Based on the mean drop size, dispersions may be classified into two categories. These are :

1) Primary dispersions in which the drop diameters are of the order of 100 microns and above (Sareen et al., 1966). In such dispersions when agitation is stopped, the drops readily settle due to gravity forces and collect at the phase boundary between the two liquids, separation finally taking place by drop/drop coalescence within the dispersion and drop/interface coalescence at the phase interface.

2) Secondary dispersions are made of sub-micron sized droplets. Unlike primary dispersions these will not readily settle to form a heterogeneous zone at the phase boundary and thus simple gravity settlers are not efficient for the separation of secondary dispersions so that other methods should be employed (Sareen et al., 1966).

To facilitate separation, the drop size distribution should be controlled to minimize the formation of secondary dispersions. However, seondary hazes are formed within a primary dispersion due to partial coalescence (Davies et al., 1970b) and these can affect the final separation.

The coalescence process is complex and relatively little work has been carried out on coalescence within droplet dispersions. Most of the literature on this subject deals with the coalescence of single drops at an interface.

3.1 Coalescence of a Drop at a Liquid Interface

The study of a single drop resting on a plane or deformable liquid/liquid interface has been the subject of many investigations. This is understandable because before the coalescence of dispersions of the type existing in engineering equipment can be predicted, all the factors involved must be identified and their significance estimated.

According to Jeffreys and Davies (1971) the single drop coalescence process takes place through five consecutive stages:

1) the approach of the drop to the interface, resulting in deformation of both drop and the interface;

2) damped oscillation of the drop at the interface;

3) the formation of a film of the continuous phase between the drop and its bulk phase;

4) drainage of the film, its rupture and removal with the initiation of the coalescence process proper, and

5) whole or partial drop transfer to its bulk phase.

The completion time for the above steps is called the coalescence time which usually consists mainly of the film drainage time (known as rest time), since other steps are relatively fast.

3.1.1 Coalescence Time Distributions

Many workers have found that the coalescence times of individual drops in a given liquid/liquid system are not constant, but if a sufficiently large number of drops are examined separately, a distribution curve is obtained. The distribution data of several investigators (Cockbain and McRoberts, 1953, Gillespie and Rideal, 1956, Nielsen et al., 1958, Charles and Mason, 1960b, Jeffreys and Lawson, 1965, Edge and Greaves, 1967) show good agreement with an equation of the type :

$$\log_e \left(\frac{M}{M_o}\right) = - C_{3.1} \left(t - \tau_{min}\right)^{m_{3.1}} \qquad (3.1)$$

where M_o is the total number of drops studied and M the number that did not coalesce in time t. The time τ_{min} is taken as an initial rest time to drain the film to a critical thickness before coalescence can occur, and $C_{3.1}$ is a rate constant dependent on the physical properties of the system and capillary waves generated by thermal and mechanical disturbances (Gillespie and Rideal, 1956) :

$$C_{3.1} = C_{3.2} \left(\frac{12\sigma}{\mu_c \phi}\right)^{0.5} \qquad (3.2)$$

$C_{3.2}$ and $m_{3.1}$ are empirical constants. The following values of $m_{3.1}$ have been found :

$m_{3.1}$	Reference	
1.0	Cockbain and McRoberts	(1953)
1.5	Gillespie and Rideal	(1956)
	Nielsen et al.	(1958)
	Charles and Mason	(1960b)
2.0	Jeffreys and Lawson	(1965)
1.75 - 3.0	Edge and Greaves	(1967)

Elton and Picknett (1957) found that the possibility of coalescence fell off continuously with increasing separation of the drop and the interface, as opposed to approaching zero at a finite film thickness as assumed by Gillespie and Rideal (1956). They reported instances where drops coalesced immediately on arrival at the interface and consequently proposed that the coalescence times would be best correlated by :

$$\log_e \left(\frac{M}{M_o}\right) = - C_{3.3}\, t^{m_{3.2}} \qquad (3.3)$$

where $m_{3.2}$ was 2 for high and 3 for low electrolyte concentrations. Jeffreys and Lawson (1965) and Jeffreys and Hawkesley (1965a) found a value of 4 for all systems with or without solute transfer between the liquid phases. Results of Davies et al.(1971) on two-component systems show $m_{3.2}$ to vary between

0.78 and 5.81.

Reproducibility of results has always been difficult because of many factors: interfacial purity (Hodgson and Lee, 1969 , Barber and Hartland, 1976), interfacial tension gradients created by the motion of fluid adjacent to the interface (Hartland et al., 1975), irregular approach of the drop to the interface, giving rise to a film of non-uniform thickness lacking axial symmetry, circulation within the drop and its homophase adjacent to the interface (Hartland, 1969a, Reed et al., 1974a,b, Riolo et al., 1975), vibrations and temperature fluctuations.

3.1.2 Factors Affecting Coalescence Times

The coalescence of a single drop at an interface is accomplished through draining and rupture of the film of the continuous phase. The factors affecting the drainage and rupture have been investigated by many authors and will be discussed below. It must however be emphasized here that the conclusions and statements of different authors in describing the effects of these factors are often conflicting and confusing.

i) Droplet Size

It is generally accepted by most authors that single drop/ interface coalescence times increase with drop diameter, but the exact relationship is not clear. Larger drops tend to flatten more than smaller ones so that the draining film is larger in area. However, the force pressing on the film is also larger and it is difficult to evaluate these two effects unless the actual drop dimensions and shape of the interface are known.

The dependence of mean coalescence time on the drop diameter can be expressed as :

$$\tau \; \alpha \; \phi^{m_{3.3}} \qquad (3.4)$$

The following values of $m_{3.3}$ have been found :

$m_{3.3}$	Reference
3.15	Charles and Mason (1960b)
1.0	Jeffreys and Hawksley (1965a)
1.0	Hanson and Brown (1967)
1.5	Lawson (1967)
2.1	Komasava and Otake (1970)
0.6-2.9	Burrill and Woods (1973b)

There are however opposing trends in the literature. Cockbain and McRoberts (1953) investigating oil/water systems containing surfactants, reported that the mean coalescence time of benzene and paraffin drops showed no marked change between ϕ = 0.98 mm and 2.67 mm but increased rapidly with decreasing ϕ below 0.98 mm. Nielsen et al (1958) reported that τ may either increase or decrease with ϕ when surfactants are present. Lang and Wilke (1971b) also found it difficult to predict the effect of drop size on τ. Their results on two-component systems reveal some systems in which τ increase with size, some that decrease with size and others which show no pattern.

ii) External Forces

Vertically externally applied forces have been shown to increase coalescence times by decreasing film drainage and increasing film areas caused by drop deformation (Hartland and Wood, 1973a, b).

Shear forces result in uneven drainage which will reduce coalescence times (Rumscheidt and Mason, 1961a,b). However, the effect is reduced by the surfactants that decrease unsymmetrical drainage (Hartland and Robinson, 1970).

iii) Density Difference

The larger the phase density difference the greater the deformation of the drop and interface (Lawson, 1967, Jeffreys and Davies, 1971). The drop flattens so that the area of the draining film is increased, whereas the hydrostatic forces causing the drainage do not increase proportionally (Jeffreys and Davies, 1971) so that the coalescence time increases. Many workers (Gillespie and Rideal, 1956, Charles and Mason, 1960a,b, Mackay and Mason, 1963, Jeffreys and Hawksley, 1965a, Davies et al., 1971, Lang and Wilke, 1971a,b) have included this factor in their models and correlations. Conflicting directional effects of $\Delta\rho$ indicated by the correlations of coalescence times (Section 3.1.3) are nevertheless noteworthy.

iv) Curvature of the Interface

Nielsen et al. (1958) observed that the coalescence time of a drop could be varied by changing the curvature of the interface; if the drop was on the concave side of the interface so that the interface curved around the drop, the coalescence times were considerably longer than when the drop was on the convex side of the interface.

v) Length of Fall to the Interface

There are contradictory reports on the effect of distance of fall to the interface. Nielsen et al. (1958), Davies et al. (1971) and Burrill and Woods (1973b) found that coalescence time was independent of the distance the drop settled whereas Lang and Wilke (1971b) reported that the length of fall could either increase or decrease the stability of a drop dependent upon mechanical disturbances produced. However, Jeffreys and Hawkesley (1965a) and Lawson (1967) suggested that the stability of a drop should always increase with increase in distance of fall since the further a drop falls before it reaches the interface the more disturbances are likely to be caused at the interface resulting in ejection of the drop and thereby film thickening and increased coalescence time. Edge and Greaves (1967) observed larger secondary and tertiary drops at an increase in distance of fall.

vi) Viscosity

Increasing continuous phase viscosity results in slower film drainage and hence longer coalescence times (Allan et al., 1961, Hanson and Brown, 1967, Lang and Wilke, 1971b). Allan et al. (1961) also observed that the film thickness at rupture decreased with increasing continuous phase viscosity. Lang and Wilke (1971b) found that coalescence time was independent of the dispersed phase viscosity when the coalescence rate-determining step was that of film thinning, but it increased with dispersed phase viscosity when the coalescence rate-determining step was that of the Taylor instability rupture. Reed et al.(1974a,b) found that the continuous phase films of much higher viscosity than the drop phase thin faster than the converse case, i.e. coalescence time increases with the dispersed phase viscosity.

vii) Interfacial Tension

A high interfacial tension results in the drop resisting deformation so that the area of the drainng film decreases and hence also the coalescence time (Lawson, 1967). However, an increase in interfacial tension also tends to inhibit the flow in the film itself, thereby increasing rest times (Jeffreys and Davies, 1971). The opposing effects of this physical property are reflected by the coalescence time correlations discussed in Section 3.1.3.

viii) Presence of a Third Component

The presence of a third component can accelerate or retard the rate of coalescence. Thus, solid substances promote coalescence when they are wetted by the drop phase because solid particles tend to form a bridge across the draining film thereby promoting its rupture. Charles and Mason (1960b) deliberately contaminated a water/benzene interface with glass beads (50 to 150 microns in diameter) and found that water drops coalesced instantaneously.

When a third substance is present in a solution of one or both of the phases its effect on coalescence process may be varied. The presence of surfactants retard coalescence (Nielsen et al., 1958, Allan et al., 1961) since they accumulate on both the drop surface and the interface with the result that the drainage rate is reduced, probably due to an increase in interfacial viscosity. Studies of the effect of surfactants on film drainage rates (Hartland, 1968, Hodgson and Lee, 1969, Hodgson and Woods, 1969) reveal that surfactants result in more uniform films, immobile interfaces, stagnated dimple central regions, and non-uniform barrier region drainage.

Finally, solute transfer into or out of the drop may occur during the coalescence process. For most pairs of immiscible liquids the addition of a third component soluble in each phase lowers the interfacial tension. Thus, when solute is transferred into the drop, the solute concentration in the film drops more rapidly than in the bulk of the continuous phase and hence the interfacial tension inside the film is greater than on the outside. The resultant interfacial tension gradient opposes the drainage so that the rate of coalescence is low. Conversely, when solute is transferred from the drop into the continuous phase the film becomes saturated before the bulk and the concentration inside the film is greater than outside. This results in a decrease in the interfacial tension locally which causes the interface in the contact zone to dilate, drawing with it part of the intervening film which promotes coalescence. Many publications (Charles and Mason, 1960b , Mackay and Mason, 1963, Smith et al., 1963, Jeffreys and Lawson, 1965) corroborating these two facts are available.

ix) Mutual Solubility

The mutually saturated phases always give longer coalescence times than the unsaturated phases (Nielsen et al., 1958) since during the transfer interfacial tension gradients are created which reduce τ.

x) Temperature and Temperature Gradients

An increase in temperature decreases continuous phase viscosity and temperature gradients weaken films, thus decreasing coalescence times (Cockbain and McRoberts, 1953, Gillespie and Rideal, 1956, Nielsen et al., 1958, Könnecke, 1959, Charles and Mason, 1960b, Jeffreys and Hawksley, 1965a, Lawson, 1967).

xi) Vibration

There are conflicting reports on the effects of vibration on coalescence times. Mahajan (1934) and Gillespie and Rideal (1956) suggested that extraneous vibrations of the kind transmitted through laboratory floors and walls tend to stabilize the draining film, thereby impeding coalescence, whereas experiments carried out by Nielsen et al. (1958) indicate that vibrations have only a slight effect on the coalescence time. Cockbain and McRoberts (1953) found that a disturbance of the interface caused by the coalescence of one drop did not affect the rate of coalescence of other drops. However, the study of Lang and Wilke (1971a,b) shows that strong vibrations (natural or induced) will reduce coalescence time, which may have a significant effect, depending on whether the coalescence rate-determining step is that of film drainage or film rupture.

xii) Electrical Effects

D.c. fields assist the coalescence of aqueous droplets (Charles and Mason, 1960b, Allan and Mason, 1961, Mackay and Mason, 1963, Brown, 1968). The application of a d.c. field results in the flattening of a drop so that the area of the draining film is increased but the forces promoting coalescence are so large that the rate of thinning is greatly accelerated. It has also been observed that strong d.c. fields eliminate stagewise coalescence (Charles and Mason, 1960b, Allan and Mason, 1961).

Brown and Mason (1965,1968) used high energy a.c.fields and found similar effects, with electric field application increasing the rate of drainage of oil film and probability of film rupture. The number of stages of coalescence and rest times of secondary drops formed were also found to decrease and the coalescence process became single-staged above a critical field strength.

3.1.3 Coalescence Time Correlations

A limited number of attempts have been made to correlate coalescence times in terms of physical properties and operating conditions. Jeffreys and Hawksley (1965a) considered the factors affecting coalescence time, estimated the significance of these factors and exponents by factorial experimentation and arrived at the following correlation for the "half-life" coalescence time $\tau_{1/2}$:

$$\tau_{1/2} = 4.53\text{x}10^5 \left(\frac{\mu_c^{1/2} \Delta\rho^{1.2}}{\sigma^2}\right) \left(\frac{Te}{25}\right)^{-0.7\mu_c^{1/2}} \left(\frac{\phi}{2}\right)^{0.02(\sigma^2/\mu_c^{1/2})^{0.55}} \cdot L_f^{0.001(\sigma^2/\mu_c^{1/2})^{0.91}} \qquad (3.5)$$

In this equation μ_c is in centipoises whereas the other quantities are in cgs units.

Jeffreys and Davies (1971) simplified the analysis by stating that temperature affected the physical properties only so that temperature, as such, need not be considered as a variable. These authors gave the following equation for the mean coalescence time, τ:

$$\frac{\tau\sigma}{\mu_c\phi} = 1.35\text{x}10^5 \left(\frac{L_f}{\phi}\right)^{0.18} \left(\frac{\Delta\rho g\phi^2}{\sigma}\right)^{0.32} \qquad (3.6)$$

It should be noted that equations (3.5) and (3.6) are restricted to a relatively narrow range of physical properties.

Davies et al.(1971) used 8 liquid/liquid sytems covering a wide range of physical properties and related the mean coalescence time as :

$$\frac{\tau\sigma}{\mu_c\phi} = 6.2\text{x}10^3 \left(\frac{\Delta\rho g\phi^2}{\sigma}\right)^{-1.14} \left(\frac{\mu_c}{\mu_d}\right) \tag{3.7}$$

The distance of fall was found to have no effect on coalescence time.

These authors gave a further correlation for drop/interface coalescence with multiple drops present at the interface, as:

$$\frac{\tau\sigma}{\mu_c\phi} = 31\text{x}10^3 \left(\frac{\Delta\rho g\phi^2}{\sigma}\right)^{-1.24} \left(\frac{\mu_d}{\mu_c}\right) \tag{3.8}$$

The opposite directional effects of various quantities in equations (3.5) to (3.8) are noteworthy.

None of these correlations seems to be very reliable since all of them are based on a limited number of experimental observations.

The order of magnitude difference between single and multiple drop coalescence times was qualitatively observed with two-dimensional arrays of drops of Robinson and Hartland (1971).

3.1.4 Drop Shape and Film Drainage

Princen (1963) and Princen and Mason (1965) pointed out that the shape of a drop approaching its homophase is a spherical cap, the depth of submergence into the interface depending on the density difference between the phases and the interfacial tension. This was later confirmed by Hartland (1967b,c,d,e, 1968), who studied viscous systems and found that the continuous phase film can be initially modelled as uniform, it drains unevenly to thin at a barrier ring along the drop contact edges and forms a dimple in the centre of the droplet. This ring and dimple behaviour has been studied previously using light scattering techniques (Allan et al., 1961, Mackay and Mason, 1963).

Hartland (1969a) has also shown by means of a force balance that the drop remains close to its equilibrium shape at all stages on its approach to a deformable interface.

Rupture has also been observed to occur at random, but mainly along the barrier ring. This was first noticed by Gillespie and Rideal (1956) and has since been explained by the slightly uneven approach of droplets to the interface (Charles and Mason, 1960b , Allan et al., 1961, Mackay and Mason, 1963, Jeffreys and Hawksley, 1965b, Hartland, 1967b,c,d). Another explanation is the presence of unknown surface active impurities (Hodgson and Lee, 1969,Hodgson and Woods, 1969). These are suggested as the cause of uneven interfacial tension gradients and interfacial mobility, which results in a stagnated film region in the centre, that is, the dimple, and rapid uneven drainage around the barrier ring, resulting in the random nature of the film rupture.

3.1.5 Mathematical Models for Film Drainage

When a drop approaches an interface, or another drop, a fluid film is formed which thins as the two interfaces are forced together. When the film becomes sufficiently thin an instability develops, the film ruptures and coalescence occurs. The critical film thickness at which rupture occurs is governed by the stability of the film (Lang and Wilke, 1971a,b). The mathematical models mentioned below are however only concerned with the rate at which a film drains.

The earlier models assume the draining film to be of uniform thickness and employ the well-known Reynolds equation (Reynolds, 1886) for the rate of drainage between two rigid parallel discs being pushed together with a force F_d. The Reynolds equation is given by :

$$-\frac{d\delta}{dt} = \frac{8F_d\ \delta^3}{3\pi n_i^2 \mu_c\ x_d^4} \tag{3.9}$$

where δ is the thickness of the film, x_d the radius of circle of contact and n_i the number of immobile interfaces.

The model proposed by Charles and Mason (1960b) on the assumption that the drop remains spherical while the interface deforms, yields a value of x_d which, for the case of a drop resting at an interface under its own weight is given by :

$$x_d = \left(\frac{\phi}{2}\right)^2 \left(\frac{2}{3}\frac{\Delta\rho g}{\sigma}\right)^{1/2} \tag{3.10}$$

The same value for x_d is predicted by the model of Gillespie and Rideal (1956) which assumes that the interface remains flat and the drop deforms.

Both models predict the same rate of film thinning which, from equations (3.9) and (3.10) for the gravitational approach of the drops, is :

$$-\frac{d\delta}{dt} = \frac{8\,\sigma^2\,\delta^3}{n_i^2\mu_c\Delta\rho g(\phi/2)^5} \tag{3.11}$$

The condition under which the assumption that the drop remains spherical will be valid is that the excess pressure within the drop, $4\sigma/\phi$, should be large compared with the hydrostatic pressure, $\phi\Delta\rho g$, and this is satisfied when the drop radius $\phi/2$ is much less than the Laplace radius $(\sigma/\Delta\rho/g)^{1/2}$ (Mackay and Mason, 1963, Hartland and Hartley, 1976).

A third model for small drops (Elton and Picknett, 1957, Chappelear, 1961) assumes that both drop and interface are deformed, the continuous phase film having a radius of curvature ϕ. The value of x_d for this case is given by (Chappelear, 1961, Mackay and Mason, 1963, Hartland and Hartley, 1976) :

$$x_d = \left(\frac{\phi}{2}\right)^2 \left(\frac{4\Delta\rho g}{3\sigma}\right)^{1/2} \tag{3.12}$$

which, upon substitution in equation (3.9) yields the rate of thinning as :

$$-\frac{d\delta}{dt} = \frac{2\,\sigma^2\,\delta^3}{n_i^2\,\mu_c\Delta\rho g(\phi/2)^5} \tag{3.13}$$

Chappelear (1961) also pointed out that the assumption of a draining film of uniform thickness disagrees with the fact that the pressure in the thinning film must decrease in the direction of flow, with accompanying variations in film thickness. It has been shown (Hartland, 1967a,c,e) that the uniform film models can be applied for the initial part of the drainage period before dimpling or film distortion occurs.

However, a thin film is normally not bounded by parallel planes. As a drop approaches an interface it develops a dimple; the film is thicker at its centre than at its edges (Derjaguin and Kussakov, 1939, Allan et al, 1961, Mackay and Mason, 1963, Hartland, 1967c, Hodgson and Woods, 1969, Burrill and Woods, 1973a,b). The first attempt at deriving equations governing the approach of a small drop to a flat interface in which the dimpling of the drop is considered was made by Frankel and Mysels (1962). Their expressions for the rate of thinning at the barrier ring and at the apex of the dimple are :

$$-\frac{d\delta_{min}}{dt} = \frac{8.3\ \sigma^2 \delta_{min}^3}{n_i^2 \mu_c \Delta\rho g (\phi/2)^5} \qquad (3.14a)$$

$$-\frac{d\delta_{max}}{dt} = \frac{87.9\ \sigma^4\ \delta_{max}^5}{n_i^2\ \mu_c (\Delta\rho)^3 g^3 (\phi/2)^{11}} \qquad (3.14b)$$

The rate of drainage predicted by equation (3.14a) is nearly equal to that given by the parallel disc approach (equation (3.11)).

Hartland and Robinson (1977) developed a more detailed model for a dimpled draining film. They considered drops of any size and assumed the film to consist of two parabolæ, joined at the point of inflection, with the radius of curvature at the apex varying with time in the central parabola and constant in the peripheral parabola. Their model, which requires a priori knowledge of radial position outside the barrier ring at which the film pressure equals the hydrostatic pressure, reduces algebraically to equations (3.14a,b) of Frankel and Mysels (1962) for the gravitational approach of small drops, but with different numerical constants. These authors also suggested a criterion for the non-uniformity of thickness in a film, based on the thickness at the centre and the barrier ring and the radius of the barrier ring.

Some authors (Hodgson and Lee, 1969, Hodgson and Woods, 1969, Burrill and Woods, 1973a,b) have analyzed the film thinning considering the presence of surfactants, and interfacial movement and tension gradients. They suggested that surfactants cause interface immobility which decreases drainage rates. In a pressure distribution study, Burrill and Woods (1969, 1973a) used light interference measurements to find a pressure distribution in the film and then calculated the film shapes.

3.1.6 Partial Coalescence

In studies of this phenomenon (Charles and Mason, 1960a, Jeffreys and Hawksley, 1962, Jeffreys and Lawson, 1965, Jeffreys and Hawksley, 1965a , Hanson and Brown, 1967, Lawson, 1967, Brown, 1968, Brown and Hanson, 1968, Davies et al.,1971) two coalescence mechanisms have been observed. In the first mechanism (Charles and Mason, 1960a) using very high speed cine photography, were able to show that during the drainage process the drop forms into a vertical column of liquid, the height of which remains virtually constant while the radius decreases. When the circumference of the liquid cylinder becomes equal to its height it behaves like an unstable jet in which a Rayleigh type disturbance can grown. Such a disturbance is concentrated at the base of the liquid column and, when its amplitude becomes equal to the radius of the column a break occurs, the remaining undrained liquid forming a new droplet - the secondary droplet. The events occurring during the partial coalescence are illustrated in the sequence A to F in Figure 3.1a. This process may be repeated several times although there is a minimum droplet size below which the coalescence becomes single-staged.

A second, more violent mechanism (Jeffreys and Lawson, 1965, Hanson and Brown, 1967) expels a secondary droplet during

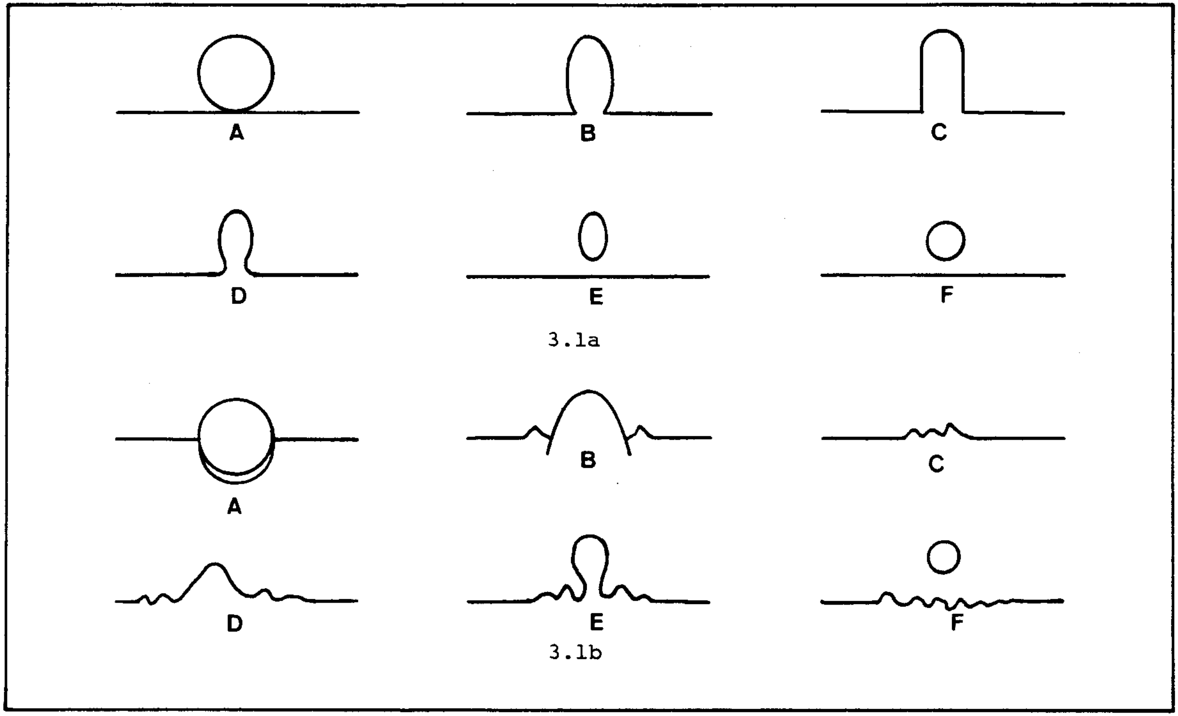


Figure 3.1 Mechanisms of Partial Coalescence

coalescence and results in a primary drop being mixed with the bulk homophase. Figure 3.2b shows the sequence A to F of the events.

The parameter determining which mechanism applies seems to be the position of the primary drop in the interface (Hanson and Brown, 1967) which, in turn, is governed by the interfacial tension, density difference and size of the drop. A submergence depth greater than 0.26ϕ results in a more violent second mechanism whilst a submergence depth of less than 0.26ϕ results in coalescence by simple drainage, that is, the first mechanism.

Charles and Mason (1960a) proposed the viscosity ratio $p'(=\mu_d/\mu_c)$ as the criterion for the occurrence of stagewise coalescence with multi-stage coalescence occurring if p' lies between 0.02 and 11. These limits are not strict as single-stage coalescence was found (Davies et al., 1971) for p' greater than 0.02. The diameter ratio, secondary to primary, has been found to vary with the viscosity ratio p' and passes through a maximum near p' = 1 (Charles and Mason, 1960a) and shows a weak dependence on primary drop size (Mackay and Mason, 1963, Hanson and Brown, 1967) and on phase viscosities (Hanson and Brown, 1967).

The number of coalescence stages increases with initial drop size (Brown and Hanson, 1966), viscosity ratio p' (Davies et al., 1971) and decreases in the presence of surfactants (Charles and Mason, 1960a) and electric fields (Charles and Mason, 1960a, Brown and Hanson, 1968). Double secondary droplet formation has also been observed (Charles and Mason, 1960a, Edge and Greaves, 1967, Davies et al., 1971). Stepwise coalescence has also been observed within droplet dispersions (Davies et al., 1970b).

3.2 Coalescence and Separation of Droplet Dispersions

Separation of liquid/liquid dispersions is an important unit operation in liquid/liquid extraction and effluent treatment processes. Coalescence and phase separation can be carried out in a range of equipment, for example, simple gravity settlers, packed columns, fibre beds and centrifuges. The following sections however refer mainly to systems utilizing gravity coalescence.

3.2.1 Gravity Settlers

A gravity liquid/liquid settler is a device used to separate a liquid/liquid dispersion into two immiscible liquid phases, one generally a light organic phase and the other a denser, aqueous phase. Gravitational separation occurs by the virtue of liquid density difference which drives the dispersed phase droplets toward the bulk homophase and causes drainage of the continuous phase from the dispersion. The droplets undergo drop/drop coalescence within the dispersion and drop/interface coalescence at the dispersion/bulk dispersed phase interface.

Gravity settlers operate in various ways (Barnea and Mizrahi, 1975a, Glasser et al., 1976) :

1) continuous horizontal settlers with wedge-shaped dispersion bands (which may not cover the entire interface);

2) continuous vertical settlers with dispersion bands up to 1500 mm thick covering the interface;

3) dilute feed dispersions (less than 15% by volume of the dispersed phase), which do not form dispersion bands;

4) dispersion feeds containing solid feeds or more than two liquid phases;

5) overloaded settlers giving incomplete separation; and

6) continuous settlers with mechanical separation aids.

Generally the aim of gravity settlers is to achieve as complete a phase separation as possible at the minimum of cost.

3.2.2 Factors Affecting the Performance of a Continuous Mixer-Settler

i) Mixer Configuration

The configuration of a mixer includes the shape of the mixing tank, the design and location of baffles and the design and location of the impeller in the mixing tank. All these combined together constitute the mixing environment and profoundly affect the velocities and flow patterns in the mixer and hence the drop size distribution produced.

The choice between cylindrical and cubic mixing tanks depends more on construction and economic considerations than on the effectiveness of mixing, which could be good in both cases. With a cylindrical design baffles are essential if vortexing is to be avoided and good mixing obtained, but in the cubic design the baffling effect is automatically achieved.

There is a wide scope for variation in impeller design, from the axial flow propeller to radial flow flat-bladed turbine, with or without shrouds. The choice on propeller would depend on achieving a balance between power consumption, extraction efficiency and entrainment (Lott et al., 1972).

Finally, the vertical position of the impeller in the mixing tank should be determined. As discussed earlier in Section 2.2.1, Skelland and Seksaria (1978) indicate that the minimum speed for complete mixing is strongly dependent on the position of the impeller in the mixing tank. However, under conditions of complete mixing the values of the interfacial area per unit volume of dispersion are independent of the position of the impeller when the ratio of the height of the impeller from the bottom of the mixing tank to the tank diameter is greater than 0.1 and less than 0.7 (Fernandes and Sharma, 1967). Since the variations in the ratio of the impeller to the mixing tank height with the range of 0.1 to 0.75 do not affect the power consumption significantly (Miller and Mann, 1944), the vertical position of the impeller in the mixing tank may be dictated by the impeller design which determines the flow patterns and internal recirculation in the mixing tank and hence the extraction efficiency (Lott et al., 1972).

ii) Mixing Regime

Liquid/liquid systems may be classified as "sensitive" or "insensitive", according to the influence of mixing energy input, i.e., the mixing intensity and/or residence time in the mixing tank (Barnea and Mizrahi, 1975d). With sensitive systems the dispersion band height increases over a wide range when the mixing time, diameter and speed of the impeller are increased. Insensitive systems are characterized by the fact that an asymptotic maximum in the dispersion band height is obtained in the normal range of operation, i.e., a mixing time of 10 to 200 seconds and an impeller speed 2 to 3 times the minimum speed for uniform dispersion (Lott et al., 1972, Barnea and Mizrahi, 1975d). Even insensitive systems will show smaller dispersion band heights when mixed for only a few seconds or without uniform mixing.

Extraction efficiency increases with increased mixing intensity until it approaches a maximum value; the extent of dispersed phase entrainment increases when the impeller speed is increased (Lott et al., 1972, Warwick and Scuffham, 1972).

All these observations are, of course, related to a given impeller design. There is not necessarily any relationship between the effects of one design of impeller with a given mixing speed and effects of another design with the same speed. It would therefore be misleading to define a settler's characteristics without a very precise definition of the mixing intensity.

iii) Phase Continuity

Dispersion band heights in settlers are substantially greater when the mixer is operating with the organic continuous dispersion than they are when the aqueous phase is continuous (Ryon et al., 1959, 1960, Warwick et al., 1971, Lott et al., 1972, Rowden et al., 1974). Though these observations are restricted to particular liquid/liquid systems it is advantageous to run a mixer/settler organic continuous because the organic entrainment in the aqueous phase, and hence the cost of solvent losses, is low. In general, the very low entrainment of the continuous phase implies that entrainment is mostly caused by the production of very fine droplets of the dispersed phase due to high shear in the mixing tank. The fact that there is still a small amount of entrainment of the continuous phase in the coalesced dispersed phase leaving the settler is due to the production of true secondary hazes during coalescence in the settler.

The stability of each type of dispersion is a factor which should be considered in the design of a mixer-settler. Ryon et al.(1959) indicate that either an oil-in-water or water-in-oil type dispersion can be made and maintained by starting the impeller with only one phase present and then starting the flow of the phase to be dispersed. Also either type can be maintained, even when the ratio of the dispersed to continuous phase is 3:1. However, the conclusions of these authors may not hold good in every situation. With a 1:1 organic to aqueous ratio the phase which becomes continuous is generally the one in which the impeller is positioned when it is started. As organic to aqueous ratio is made progressively greater or less than unity, the tendency is then natural for the phase which is present in larger quantity to become the continuous phase. There are other factors to be taken into account, for example, the mixing speed, construction materials of the tank and the physical properties of the liquid/liquid system (see Section 2.2.2).

iv) Feed Dispersion Concentration (Phase Ratio)

The feed dispersion concentration is very important to industrial operation since it can be adjusted by internal recycling between the mixer and the settler. Dispersion band height, extraction efficiency and entrainment, both of aqueous in the organic phase and of the organic in the aqueous phase have been found to be affected by feed dispersion concentration.

The data published by Ryon et al.(1960) leads to the inferred extrapolation that the dispersion height depends only on the dispersed phase throughput per unit area, Q_d/R, while the continuous phase throughput per unit area, Q_c/R, has a negligible effect. These authors proposed that a unique plot of dispersion band height, H, versus Q_d/R could be obtained with various values of feed dispersion concentration, ε_f :

$$H = C_{3.4}\left(\frac{Q_d}{R}\right)^{m_{3.4}} = C_{3.4}\varepsilon_f^{m_{3.4}}\left(\frac{Q}{R}\right)^{m_{3.4}} \qquad (3.15)$$

The data of these authors gave $m_{3.4} = 2.5$ and it follows that the capacity of a continuous settler in terms of total throughput for a given H is inversely proportional to ε_f.

The relationship given by equation (3.15) has been confirmed by Golob and Modic (1977). Their data on water/Shell Sol system gave $m_{3.4} = 3.1$. Gondo et al. (1968, 1969) correlated the height of the dispersion band (15 to 400 mm) with the feed throughput, the dispersion concentration (0.3 to 0.6) and the speed N of the mixer impeller (7.2 to 10.3 rps) giving

$$H \ \alpha \ N^{2.8} \ \varepsilon_f^{4.9} \ \left(\frac{Q_c+Q_d}{R}\right)^{3.1} \qquad (3.16)$$

which is in general agreement with the results of Ryon et al. (1960), but indicates that H would decrease if the continuous phase throughput is increased, all other variables being kept constant. However, the exponent of ε_f is 4.9 instead of 2.5, thus changing the relationship between the capacity of a continuous settler and ε_f.

Rowden et al. (1974) studied in detail the effects of changes in the feed dispersion concentration under both organic and aqueous continuous mixer conditions. Their experimental results on an LIX/copper system in vertical settlers showed a marked dependence of settler performance on feed dispersion concentration. Their important conclusions for the single stage experiments with constant total throughput are :

1) There exists a "preferred" packing ratio in a dispersion band which results when the operating dispersed/continuous

phase ratio is 2:1. At this "preferred" packing ratio the dispersion band height passes through a maximum;

2) Extraction efficiency with recycle is markedly improved when recycle results in an increase in proportion of the dispersed phase present in the mixer;

3) Under organic continuous mixer conditions, organic entrainment in the aqueous phase is governed by the settler operation and the values of the organic entrainment are almost independent of the operating organic/aqueous ratio. Aqueous entrainment in the organic is maximum at highest operating organic/aqueous ratio and decreases exponentially with the decrease in organic/aqueous ratio.

4) Under aqueous continuous mixer conditions, organic entrainment in the aqueous phase is governed by the mixer operation. Organic entrainment is maximum at the lowest organic/aqueous ratio and decreases exponentially with increasing organic/aqueous ratio.

These authors presented arguments to support the above mentioned conclusions. There were however not able to explain the trend of aqueous entrainment in the organic phase under aqueous continuous mixer conditions.

Barnea and Mizrahi (1975d) pointed out that the result of an increase in ε_f may not be constant and a minimum settler capacity may be expected in certain systems for a definite ε_f. Their results of an IMI phosphoric acid process show that settler capacity based on total throughput decreases with an increase in ε_f until a minimum is reached (for $\varepsilon_f = 0.5$); the capacity then increases again as ε_f is increased. These authors also showed that variations in feed dispersion concentration would alter the exponent $m_{3.4}$ of equation (3.15) in an inconsistent fashion, unless the settling conditions are within creeping flow region ($m_{3.4} \simeq 2.5$). For settling conditions in the creeping flow range variations in ε_f do not affect the value of $m_{3.4}$ as is indicated by the data of Ryon et al. (1960).

v) Temperature

An increase in temperature results in increasing the settler's capacity (Ryon et al., 1960, Ryon and Lowrie, 1963, Mizrahi et al., 1974, Barnea and Mizrahi, 1975d). As a rough rule of thumb, settler capacity can be doubled when operated at 40°C instead of 20°C (Mizrahi et al., 1974, Barnea and Mizrahi, 1975d). For a given total throughput and feed dispersion concentration, the smaller value of dispersion band height at a higher temperature is attributed to the combined effect of the following factors (Barnea and Mizrahi, 1975d) :

1) The coalescence times (drop/drop and drop/interface) decrease with decreasing continuous phase viscosity as the temperature increases, so that the rate of coalescence increases;

2) The minimum drop size which can settle countercurrently to the continuous phase also decreases (for a given throughput) with the decrease in continuous phase viscosity.

3) If the dispersion is produced in a mechanical mixer (normal case) the average drop size of the feed dispersion also increases since it is the resultant of the dynamic equilibrium of the two mechanisms: droplet break-up and coalescence in the mixing tank, the latter process being much more temperature-dependent than the mechanical shearing process and consequently the dynamic equilibrium is shifted towards coarser size distributions.

An increase in operating temperature also reduces the entrainment in both phases (Ryon et al., 1960, Manchanda and Woods, 1968).

vi) Settler Configuration

First, the size and positioning of the dispersion inlet is important. Horizontal settlers normally employ full width inlet weirs to eliminate turbulence and re-entrainment of the settled phases in the region of the settler inlet (Warwick et al.,1971, Lott et al., 1972). Davies et al.(1970a) found that by replacing the plain inlet pipe by a divergent rectangular duct, the capacity of the settler increased by up to 50%. The importance of the location of the settler inlet with respect to the dispersion band has been discussed by many authors (Ryon et al., 1960, Manchanda and Woods, 1968, Davies and Jeffreys, 1970, Davies et al., 1970a, Lott et al., 1972, Barnea and Mizrahi, 1975b). It has been shown (Davies and Jeffreys, 1970, Davies et al., 1970a) that by varying the level at which the dispersion enters the settler, the dispersion band height can be varied for a given throughput, the minimum dispersion band height being achieved when the inlet is into the dispersion band and close to the coalescing interface. Barnea and Mizrahi (1975b) have been quite specific in detailing the location of the settler inlet in stating that it should be at the boundary between dense and even concentration layers since feeding near the passive interface results in a thicker dispersion band due to the disturbance of the concentration profile. Horizontal settlers generally also include an impingement baffle immediately after entry to the settler to reduce jetting of the incoming dispersion into the coalescence region (Brown and Hanson,1966, Lott et al., 1972, Warwick and Scuffham, 1972, Roberts et al., 1979).

The flow pattern in the settler is the next important consideration and has a significant effect on both settler area required and entrainment produced. Picket fence baffles are sometimes used in a horizontal gravity settler, being situated at intervals along its length. A picket fence baffle consists of two or three rows of vertical slats placed one behind the other across the width of the settler, being placed so that they are located opposite open places in adjacent rows. A picket fence baffle is not only useful in distributing the flow laterally across the settler but also damps out wave motions which would otherwise result in organic or aqueous carryover at the weirs (Warwick et al., 1971, Roberts et al., 1979). A picket fence can also act as an aid to coalescence if it is made of a material which is wettable by the dispersed phase (Warwick et al.,1971, Lott et al.,1972, Warwick and Scuffham,1972). Detailed settler flow pattern studies (Hanson and Sharif, 1970, Barnea and Mizrahi, 1975b) have shown that most of the dispersed phase has a low residence time in the dispersion band with a long "tail" of smaller droplets in the bulk of the dispersion band. Prevention of this "tail" would result in a marked increase in settler capacity. Finally, full-width organic and aqueous outlets are also used in horizontal settlers to reduce channelling near the end of the settler (Warwick et al.,1971, Lott et al., 1972).

3.2.3 Settler Design and Modelling

Most settler research work has been directed towards empirical design, while comparatively little has been done on the actual modelling of settlers.

Settler studies have been divided into single settler and multi-stage mixer-settler units, the design of which has been based on complex hydraulic balances without detailed design of settlers (Williams et al., 1958, Treybal, 1966). Settler sizes have usually been specified by rule of thumb, so that these units are often larger and hence more expensive than is necessary.

Three different design criteria have been commonly used to scale up pilot tests to industrial use: the residence time method, the overflow velocity method and the dispersion height method. In the residence time method the equipment size is calculated to allow the dispersion a plug-flow residence time of from 5 to 300 minutes, so that the dispersed droplets can travel to the interface and coalesce (Perry, 1963, Oliver,1966, Manchanda and Woods,1968). These plug-flow residence times are based on past experience rather than on theory. Furthermore, this method takes neither the geometry of the settler nor the flow patterns within the settler into account.
The overflow velocity method (Hart, 1947a,b, Clarke and Davidson, 1962) is based on the assumption that the rate of separation is controlled by the settling rate of dispersed drops. Design is based on a time sufficient to allow for the drops to travel to the interface before leaving the settler. This method is

particularly suitable for very dilute dispersions which are generally settling rate-controlling processes. The dispersion height method (Ryon et al., 1959, 1960, Ryon and Lowrie,1963) is based on the assumption that the rate of primary separation is controlled by the rate of coalescence of the dispersed phase droplets, rather than by the rate of settling, as was assumed in the overflow velocity method. In this case a uniform thickness is assumed to exist over the cross section of the settler and a maximum allowable thickness is arbitrarily chosen. The dispersion height, as a function of total throughput, is determined for the particular liquid/liquid system by pilot plant experiments and the throughput selected to produce a dispersion height which is less than the maximum allowable.

The bulk of the studies which have been conducted on continuous settlers have utilized vertical settlers. No doubt this is due to their simplicity and the fact that their configuration is usually similar to that used in batch settling experiments. Ryon et al. (1959,1960) and Ryon and Lowrie (1963) were the first to conduct extensive studies of vertical settlers. The dispersions were formed in a variable power input mixer and passed continuously to one of a variety of settlers ranging in diameter from 152 to 1219 mm. After the phase separation the two streams were analyzed for entrainment and then recycled back to the mixer. These authors found that coalescence took place primarily at the interface between the dispersion and the bulk dispersed phase and, to a smaller extent, within the dispersion band. In addition, the height of the dispersion band was found to increase exponentially with dispersed phase throughput per unit settler area (equation (3.15)) and showed only a small effect of the phase ratio for both aqueous and solvent continuous dispersions. Therefore, these authors suggested that scale-up could be based on constant total throughput per unit settler area and constant dispersion height.

Barnea and Mizrahi (1975a,b,c,d) presented a detailed study of vertical gravity settlers. Based on the shape of hold-up profiles they reported two distinct main zones in a dispersion band, namely, a dense zone near the coalescence front and an even concentration zone, i.e. a zone of roughly constant hold-up. The dense zone occupies only 10-20% of the dispersion band and the dispersed phase hold-up is much higher than that of the feed, increasing sharply toward the coalescence front. The even concentration zone occupies 70 to 90% of the dispersion band and is characterized by a moderate and linear change in hold-up; near the settling front the hold-up falls sharply to some low value. The thickness of the even concentration zone is controlled by the hindered settling of droplets, as well as by drop/drop coalescence (in random conditions) of the smallest size fraction of the feed droplets. The role of this zone is to provide the residence time necessary for the smallest drops in the feed to grow by interdrop coalescence and settle counter-currently to the continuous phase. These authors presented statistical modelling of interdrop coalescence and combined this with a semi-theoretical expression for hindered settling of droplets to develop the following expression for the steady state dispersion band height :

$$H = C_{3.5}\left(\frac{Q}{R}\right)^{m_{3.5}} \qquad (3.16\,a)$$

where Q is the total throughput and the constant $C_{3.5}$ is a function of feed dispersion concentration (phase ratio). These authors also pointed out that a plot of log(H) versus log(Q/R) may be an upwards concave curve for a wide range of Q/R, the degree of curvature depending both on the absolute span and on the different combinations of variables. However, in the particular case when the droplet settling is within the creeping flow range, such plots are straight lines with a slope of about 2.5.

Continuous settling results of many other others (El-Roy and Gonen, 1964, Lowes and Larkin, 1967, Naylor and Larkin,1971, Warwick et al., 1971, Lott et al., 1972, Mizrahi and Barnea, 1973, Drown and Thomson,1977) also seem to be well correlated using equation (3.16).

Stönner and Wöhler (1975) reported another equation representing settling of the form :

$$\frac{Q_d}{R} = \frac{H}{C_{3.6} + C_{3.7}H} \tag{3.17a}$$

which may be re-written as :

$$\frac{H}{Q_d/R} = C_{3.6} + C_{3.7}H \tag{3.17b}$$

or

$$H = \frac{C_{3.6}Q_d/R}{1 - C_{3.7}Q_d/R} \tag{3.17c}$$

where $C_{3.6}$ and $C_{3.7}$ are empirical constants. Equation (3.17c) shows that Q_d/R has an upper limiting value. However, Stönner and Wöhler do not confirm the validity of this limiting value equation with experimental results.

Wilke and his co-workers (Graham, 1962, Epstein and Wilke, 1963, Sweeney and Wilke, 1964) conducted extensive studies of horizontal settlers. Using a water/AROCLOR system the dispersions were prepared by turbulent flow of the phases in a pipe section under conditions which generally led to multiple dispersions. These authors concluded that the important design variables were the total throughput and the extent of mixing of the dispersion entering the settler. In one of these studies, Epstein and Wilke (1963) measured the velocity of the dispersion by visually timing drops in the dispersion as they moved over fixed distances and found that,near the entrance of the settler, the dispersion moved at a velocity greater than the average velocity of either the water or the AROCLOR phase. Close to the end of the dispersion zone (near exit ports) the velocity of the droplets decreased rapidly and finally approached zero as the dispersion disappeared. Sweeney and Wilke (1964) employed a baffle at the entrance to the settler and concluded that once the entrance velocity has reached a high enough value it caused a more difficult separation. They also measured the dispersion band thickness within the settler and reported that at low throughputs the thickness decreased with the distance down the settler, but at high throughputs the thickness increased with the distance.

Jeffreys et al.(1967) were the first to present a quantitative model for liquid/liquid separation in a horizontal gravity settler for the case of a wedge-shaped dispersion band. This used the concept of coalescence stages, in which the droplets attain face-centred cubic configuration within the wedge and then "lose" one row of droplets to the coalescence front, simultaneously halving the total number of drops in a stage by interdrop coalescence. Predictions of wedge lengths agreed reasonably well with those observed in a laboratory-scale settler. However, there are limitations inherent in the model. The analogue that a row or column of drops will coalesce at some characteristic time is not physically justifiable; in practice continuous coalescence takes place throughout the bed. Furthermore, drop/drop and drop/interface coalescence times were assumed to be equal, which is not generally true.

An alternative approach to the modelling of a wedge-shaped dispersion was proposed by Jeffreys et al.(1970a,b). This differential model illustrated the relative effects of drop/drop and drop/interface coalescence and predicted wedge length, mean drop size and wedge depth for the kerosene/water system with either phase dispersed.

A modification of the above was proposed by Vijayan and Ponter (1974,1976) to further investigate the relative contributions of drop/drop and drop/interface coalescence processes to the size of the wedge. A deterministic model coupled with the differential model of Jeffreys et al.(1970a,b) was presented but experimental difficulties in measuring the ratio of drop/drop to drop/interface coalescence time prevented an accurate evaluation of this model.

Drown and Thomson (1977) observed three distinct regions for the dispersion wedge mode of operation, namely, an entrance region, a dispersion region and an exit region. The entrance region consisted of an expanding two-phase jet which not only entrained the surrounding fluid but also resulted in backmixing circulation patterns. No coalescence occurred in this region since the drops were still fluidized. The entrance length, L_e, defined as the distance from the inlet port, where circulatory flow caused by the entrance jet ceased to exist was correlated by :

$$L_e = 1.7\left(\frac{d_e^{1.5}}{\sigma^{0.5}}\right)\left(\rho_m^{0.5} V_e\right) \qquad (3.18)$$

The dispersion zone was defined as the region extending from the terminus of the entrance region to the point where the dispersion zone came under the influence of the exit ports. The length of the dispersion region could be calculated by using momentum and material balances for the two bulk fluids. The fluid mechanic patterns in the exit region were characterized by a "flood-point" parameter, defined as the ratio of the exit velocity to the vertical distance between the top (or bottom) of the dispersion zone and exit port.

Gel'perin et al.(1972) characterized the phase separation efficiency by entrainment levels, determined from the samples taken at the exit ports of horizontal settlers. The entrainment values, both of the aqueous in organic phase and organic in the aqueous phase, were correlated by using batch separation profiles and primary break time determined in a measuring cylinder, and the overall residence time (settler volume divided by the total volumetric flow rate) in the continuous settler. In practice, because of relatively low throughputs the dispersion wedge mode of operation has been discarded in favour of thick dispersion bands or mechanically aided settling.

A number of workers have tried to reduce the scale of pilot work and the cost involved by attempting to relate observations of batch to continuous settler performance. Transposition of batch profiles into continuous characteristics is however difficult, since the hold-up and drop size profiles are not the same in both cases. If batch and continuous settling are to be related the mechanisms controlling sedimentation and coalescence in two types of dispersions must be clearly understood.

Mizrahi and Barnea (1970) obtained a correlation between the nominal settler capacity $(Q/R)_N$ corresponding to an arbitrary H, and the standardized batch separation time t_B. For the system isoamyl alcohol/HCl/water the following relationship resulted :

$$\left(\frac{Q}{R}\right)_N = C_{3.8} t_B^{-0.87} \tag{3.19}$$

where $C_{3.8}$ is a constant.

Barnea and Mizrahi (1975d) used the above approach and related the nominal settler capacity ($m^3 h^{-1} m^{-2}$) to a value of H of 500 mm and the standardized batch separation time t_B (seconds) to an initial height of 300 mm. With the units used, the slopes were (-0.905) and (-0.87), the $C_{3.8}$ values being 1064 and 888 respectively for aqueous continuous and organic continuous dispersions. It should be noted that these empirical figures depend on the phase systems and arbitrary definitions.

Golob and Modic (1977) suggested that a batch test should be performed under the same conditions (mixing intensity, temperature, phase ratio etc.) and at the same dispersion height as chosen for the continuous band height. They defined a batch separation time as :

$$t_{BS} = \frac{h_{co}}{r_c} \tag{3.20}$$

where h_{co} is the initial height of the coalescing interface relative to the final undisturbed interface and r_c is an average coalescence rate of the dispersed phase obtained by measuring the position of the coalescence front as a function of time and determined in an interval where it is found to be approaximately constant. The batch separation time thus obtained can be used to calculate the nominal settler capacity by the following equation :

$$\left(\frac{Q}{R}\right)_N = H t_{BS}^{-1} \tag{3.21}$$

Godfrey et al.(1979) carried out separation tests on water/ LIX 64N-Escaid 100 and kerosene/water systems in both batch and continuous operated mixers. They showed that the tests conducted in a batch mixer can lead to serious underdesign of the settler, whereas data from a flow mixer can be used with confidence. The two conditions of operation affect the rate of separation markedly; the presence of haze in batch tests is associated with a faster coalescence rate than that observed in a flow mixer. Haze produced during start-up of the mixer in a flow system is gradually washed out and the coalescence rate in the mixer on shut-down slows down.

Vieler et al. (1979) presented an internal age-distribution model to relate a batch settler with a completely mixed continuous steady-state settler. The model assumes that the internal phase-disengagement is a function of age as well as the system properties (phase ratio, dispersion height, etc.) and highlights the fact that for accurate correlation between two types of experiments, exactly the same feed must be used for both. These authors attempted to clarify the difficulties in going from batch to continuous experiments, and pointed out that a wide series of experiments were needed to be performed for the further evaluation of the model.

Another attempt to correlate batch and continuous settling was made by Stönner (1981). Continuous and batch-settling equations of this model have been explained by Stönner and Wiesner (1980), Stönner (1981) and Hartland (1982). A reaction kinetic model based on the following assumptions is used :

1) steady state dispersion in the continuous settler is perfectly mixed;

2) feed entering the continuous settler consists of two types of drops - inactive (small) and active (large) ;

3) inactive drops react (coalesce) with each other within the dispersion band and produce active drops;

4) all the active drops react (coalesce) only with the active interface.

If θ_o denotes the fraction of inactive drops in the feed, k_b the reaction rate constant for inactive drops to produce active drops, and k_i the reaction rate constant for the active drops to coalesce with the active interface, the steady-state dispersion height H is given by :

$$\frac{H}{Q_d/R} = \frac{H}{k_i} + \frac{\theta_o}{\varepsilon k_b} \qquad (3.22)$$

where ε is the average hold-up of the perfectly mixed dispersion. θ_o, k_b and k_i could be determined by using batch decay data and steady-state dispersion height of a continuous settler predicted (Stönner,1981). The equation governing decay of a batch dispersion

$$- \frac{d(h\varepsilon)}{dt} = k_i \; (1 - \frac{h_o \; \varepsilon_o \; \theta_o}{h \; \varepsilon} \; e^{- k_b t} \;) \qquad (3.23)$$

is numerically integrated by using appropriate estimates of the parameters θ_o, k_b and k_i. For every data point of the batch experiment the deviation $(h_{exp} - h_{pred})^2$ is calculated and summed up; the parameters θ_o, k_b and k_i are varied until the sum of squares of the residuals becomes suitably small.

Stönner (1981) calculated θ_o,k_b and k_i from the batch test of Barnea and Mizrahi (1975d) but presented no comparison between predicted and experimental values of the steady-state heights reported by Barnea and Mizrahi.

3.2.4 Coalescence Aids

The main problem with existing settlers such as those used in various hydrometallurgical applications is their large size. This means a relatively high capital cost and a large solvent inventory content which can represent a substantial unproductive investment. Consequently, over the past few years a number of attempts have been made to promote coalescence within the settler by the use of baffles, or a wide variety of coalescence-promoting surfaces. Examples are : baffles (Davies et al., 1970a); packing (Ryon and Lowrie,1963, Davies and Jeffreys,1969,Davies et al. 1972); mesh (Mumford and Thomas, 1972, Jackson et al., 1974);

horizontal or inclined tray assemblies (Mizrahi and Barnea, 1973) and picket fences (described in Section 3.2.2), vertical baffles and plane gauze internals in combinations (Roberts et al., 1979). It has been established that the coalescer material should be preferentially wetted by the dispersed phase (Davies and Jeffreys,1969). The action of solid material wetted by the dispersed phase is to transform the drops into liquid films which flow over the surface.

However, the presence of solids and crud in most practical situations tend to block the surface and promote flooding of the system. Under these circumstances, the removal of the coalescing surface for cleaning with its attendant nuisance value and necessity for stopping production can lead to costs which might outweigh the advantages gained through the settler compactness. Another problem is increased entrainment resulting from secondary droplet formation produced by the rapid coalescence at preferentially wetted surfaces (Jackson et al., 1974).

A limited number of attempts have been made on the separation of dispersions by using electric fields. Brown and Hanson (1965) studied the use of an a.c. field in the settling compartment of a single-stage mixer-settler. By altering the phase ratio of the feed a water-in-oil or an oil-in-water dispersion could be produced. It was found that the application of the field markedly increased the rate of coalescence of a water-in-oil dispersion but had no effect on the oil-in-water type. Bailes and Larkai (1981) studied the effect of d.c. fields on water-in-oil dispersions, using again a single-stage mixer-settler unit. The dispersion leaving the mixer was passed through an electric coalescer before being discharged into a conventional gravity settler. In this way the dispersion height in the gravity settler was dependent on the effectiveness of the electric coalescer. Their study shows that pulsating d.c. fields are more effective than constant d.c.fields in separating liquid/liquid dispersions, the extent of phase separation depending on the applied voltage amplitude. In another publication the same authors (Bailes and Larkai,1982)show that for a given thickness of electrode coating and a given liquid/liquid system there exists a unique optimum frequency of the pulsed d.c.field at which best separation is obtained. This optimum frequency has been shown to depend on the interfacial relaxation between the insulating coating and the continuous phase.

3.2.5 Coalescence in Spray Columns

Whilst the performance of a spray-type liquid/liquid extraction column from the standpoint of mass and heat transfer has received considerable attention (Garwin and Smith, 1953, Letan and Kehat, 1967, 1968, Loutaty et al., 1969, Ferrarini, 1972, Bühler, 1977), not much work has been done on predicting coalescence rates, bed height etc. of a droplet dispersion at the phase boundary. An understanding of these should be important, not only in the operation of spray columns but also in all extraction equipment. A spray column provides the advantage that by carefully designing the drop distributor an even drop size can be obtained at the bed inlet which considerably simplifies any analysis, and by observing the drop size distribution at the phase boundary gives an indication of the extent of interdrop coalescence within the dispersion.

Smith and Davies (1970) carried out experiments on 8 liquid/liquid systems using a spray column. The hole size, pitch and thickness of the distributors were carefully chosen to minimize the variation in drop size and prevent the formation of small secondary drops. Wall effects were studied by coating part of the inside surface of the column with dimethyl dichloro silane. They reported that the dispersion band thickness was always greater when the dispersed phase wetted the column. It is however contrary to the conclusions of Ryon et al. (1959) who suggested that maximum separation efficiency was obtained in settlers when the dispersed phase wetted the surface of the vessel. The correlation of Smith and Davies for the dispersion band thickness as a function of relevant variables for the case when the dispersed phase wets the column walls is :

$$\frac{H}{\phi_o} = 3499\left(\frac{Q_d/R\cdot\mu_c}{\sigma}\right)^{0.846}\left(\frac{\Delta\rho g\phi_o^2}{\sigma}\right)^{-0.878}\left(\frac{\mu_d}{\mu_c}\right)^{0.770} \quad (3.24)$$

And for the case when the dispersed phase does not wet the column walls :

$$\frac{H}{\phi_o} = 2564\left(\frac{Q_d/R\cdot\mu_c}{\sigma}\right)^{0.823}\left(\frac{\Delta\rho g\phi_o^2}{\sigma}\right)^{-0.862}\left(\frac{\mu_d}{\mu_c}\right)^{0.773} \quad (3.25)$$

In a deterministic model the same authors (Smith and Davies, 1972) assume a plug flow through a column with drop/drop coalescence depending on drop diameters and taking place between drop pairs of particular sizes. From an elemental balance and the use of drop/interface and drop/drop coalescence models they derived the following equation for the dispersion band height in terms of dispersed phase throughput, initial drop size and physical properties :

$$\frac{H}{\phi_o} = 1510\left(\frac{Q_d/R\cdot\mu_c}{\sigma}\right)^{1.10}\left(\frac{\Delta\rho g\phi_o^2}{\sigma}\right)^{-1.38}\left(\frac{\mu_d}{\mu_c}\right)^{1.13} \quad (3.26)$$

with a correlation coefficient of 0.86. At low dispersed phase flow rates (small band heights), the deviation between theory and experiment was quite high, since their assumption of random distribution of drop sizes at any plane in the bed from the inlet becomes invalid.

Doulah and Davies (1974) considered the dispersion band to consist of a series of droplet queues. The arriving droplets choose between adjacent queues equally at random and leave via interdrop and drop/interface coalescence. The birth-death equations relating the probability of finding M droplets in a queue was used in a complex Monte Carlo simulation procedure to calculate queue length and hence bed depths. It was found that the majority of the predicted queues were greater than the experimental values, which was explained by the method, employed to account for interdrop coalescence and droplet interactions, and the simplified structure assumed for the droplet arrangement within the dispersion band. The predictions of this statistical model were as good as those of the deterministic model of Smith and Davies (1972).

Allak and Jeffreys (1974) used a refractive index matching technique developed by Hartland (1969b) to follow the separation process occurring inside thick dispersion bands in the coalescence section of a spray column. By matching the refractive index of each phase, the dispersion became transparent and one or more coloured drops were released into the band which allowed the drop behaviour inside the dispersion band to be followed. A second method used in their investigation was to generate colour in the drops, in situ, at particular positions in the band by dissolving a small quantity of a phototropic dye in one or the other of the phases and irradiating the particular section of the dispersion band to generate the coloured drops. From the experimental observations they reported that there were three distinct zones in such a dispersion band, namely :

1) a flocculating zone;
2) a packing zone;
3) a coalescing zone.

The significant process determining the thickness of the dispersion band was found to occur in the packing zone. Here the drops were pressed together and deformed into the shape of pentagonal dodecahedra. Interdrop coalescence took place by drainage of the continuous phase film separating the drops. They substantiated this observation by a simple mathematical model, developed by Hartland and Barber (1974) for a foam of gas bubbles coalescing at an interface, based on the size and shape of the drops in the band, the frequency of interdrop coalescence expressed in terms of the physical properties of the system, drop size and critical film thickness of the continuous phase film at rupture. Furthermore, the thickness of the dispersion band was observed to depend on the inlet drop size and dispersed phase throughput. The experimental results were correlated by a dimensional analysis, the predominant group being the capillary number $(Q_d/R \cdot \mu_c/\sigma)$, suggesting that the drainage of the continuous phase film controls the thickness of the dispersion band.

Hartland and Vohra (1978) assumed that the drops move in plug flow through a dispersion and presented models which describe the behaviour of growing, decaying and steady-state dispersions in terms of the dispersed phase throughput per unit area, Q_d/R, initial drop size, ϕ_o, the average hold-up of the dispersion band ε, and the coalescence times between the drops, τ_b and at the disengaging interface τ_i. They arrived at the following relationship for the height, H, of a steady state dispersion :

$$H = \frac{6\, Q_d/R \cdot \tau_b}{\varepsilon} \log_e \frac{3\; Q_d/R \cdot \tau_i}{2\; \phi_o} \tag{3.27}$$

Using the steady state model, the values of τ_b and τ_i were experimentally measured for the water/butyl acetate and water/isoamyl acetate systems, being then used to predict the rates of growth and decay which agreed well with the observed variations.

The model of Hartland et al.(1978) which predicts the variation in hold-up and drop size in a steady state dispersion, is based on the assumptions that the coalescence time, τ_b, between the drops is constant and that the drops are fluidized at each cross-section in the dispersion. The variation in the dispersed phase hold-up ε_z and the drop size with depth z in the dispersion was correlated by :

$$\log_e\left(\frac{1/\varepsilon_{zo} - 1}{1/\varepsilon_z - 1}\right) = \log_e\left(\frac{\phi - \sqrt{C_{3.9} Q_d/R}}{\phi_o - \sqrt{C_{3.9} Q_d/R}}\right) = \frac{z}{6\; Q_d/R \cdot \tau_b} \tag{3.28}$$

where $C_{3.9}$ is a constant dependent on the density difference, continuous phase viscosity and a particle shape factor.

These authors tested their model on three liquid/liquid systems and obtained good agreement between experiment and theory.

4. PREDICTION OF DROP SIZE AND DISPERSED PHASE HOLD-UP IN SPRAY AND PULSED SIEVE-PLATE LIQUID/LIQUID EXTRACTION COLUMNS

Knowledge of hydrodynamic parameters, namely, the drop size, hold-up of the dispersed phase and backmixing coefficients, together with the actual mass transfer rates is necessary in the design and scale-up of liquid/liquid extraction columns. Reliable correlations and/or models on the hydrodynamic parameters could permit the design of columns for new liquid/liquid systems without extensive pilot scale tests, provided the system properties (density, viscosity, interfacial tension etc.) are known.

4.1 Correlations for Drop Size in Spray Columns

In spray columns the drops are formed by a distributor which may be a perforated plate or set of nozzles. Drop formation mechanisms were discussed in Sections 2.1.1 - 2.1.3. At low nozzle velocities the drops are formed at the tip of the nozzle (single drop region); by increasing the nozzle velocity a cylindrical neck of the dispersed phase appears (for $v \geq v_j$) and drops are formed by jet disintegration (jetting region). Beyond the critical velocity the drop formation is less uniform; finally the jet break-up point retreats to the tip of the nozzle and a non-uniform spray of tiny droplets results.

4.1.1 Single Drop and Jetting Regions

Correlations for the drop size can be developed in terms of the nominal nozzle velocity, v, and the physical properties of the liquid systems. For low viscosity liquids the relationship between the Sauter mean drop diameter ϕ_{32} and the variables v, d, $\Delta\rho$, σ and g could be written as :

$$\frac{\phi_{32}}{d} = C_{4.1}\, We^{m_{4.1}}\, Eö^{m_{4.2}} \qquad (4.1)$$

where $We = \Delta\rho d v^2/\sigma$ and $Eö = \Delta\rho d^2 g/\sigma$. The values of We and Eö

Table 4.1 Systems Investigated

Source	No.of data points	Phases Dispersed	 Continuous	ρ_d kg/m^3	ρ_c kg/m^3	μ_d mPa s	μ_c mPa s	σ mN/m	ϕ_{32} mm	We	Eö	Fr
Horvath (1976)	104	o-Xylene	Water	880.2	998.96	0.81	1.00	30.7	2.56-5.28	0.02-0.55	0.04	0.65-14.49
Vedaiyan (1969)	85	Methylisobutylketone	Water	795.4	991.7	0.6656	0.8494	8.8	2.20-5.76	0.01-2.13	0.22-4.94	0.00-7.03
	20	Isoamylalcohol	Water	826.9	990.6	2.7463	1.0090	4.9	2.70-4.06	0.04-1.51	0.33-2.76	0.01-1.62
	56	Benzene	Water	865.0	995.6	0.6057	0.7990	24.3	3.97-9.25	0.01-1.27	0.21-0.72	0.02-5.84
	50	Water	Carbontetrachloride	997.7	1582.6	0.8736	0.9484	42.4	3.81-5.49	0.02-3.59	0.54-1.14	0.02-6.20
Garwin and Smith (1953)	65	Benzene	Water	820.7-874.3	981.0-997.8	0.3270-0.6095	0.4507-0.8647	30.2-34.1	5.84-8.35	0.07-0.65	0.33-0.54	0.19-1.26
Loutaty et al.(1969)	46	Kerosene	Water	780.7-805.7	986.4-993.6	0.7667-1.0783	0.5295-0.6963	44.5	3.14-4.69	0.08-2.15	0.07-0.08	1.05-28.30
Henton (1967)	4	Methylisobutylketone	Water	799.5	997.1	0.8252	0.8937	8.82	2.41-3.94	0.66-1.30	0.40-2.25	0.38-3.25
Miller and Pilhofer(1976)	13	Toluene	Water	866.9	1001.0	0.627	1.003	36.0	2.22-4.39	0.33-1.22	0.03-0.09	3.74-41.22
Bühler (1977)	22	Spindle Oil	Water	788.4-803.7	983.5-994.9	1.1535-1.6391	0.4807-0.7926	24.2-28.7	4.94-5.90	0.51-1.42	0.59-0.71	0.80-2.29
Kumar and Hartland(1982)	10	Water	60% Paraffin Oil and 40% Toluene	998.23	866.37	0.9924	4.0969	40.5	1.84-4.42	0.06-0.38	0.02	4.25-25.05
	9	Water	Amylalcohol	994.30	816.90	1.1131	4.0231	5.2	1.60-2.26	0.01-1.38	0.16	0.09-8.67

were calculated for 484 data points taken from 8 different data sources. These are listed in Table 4.1 along with the physical properties and range of drop diameters. The analysis was restricted to the velocities below the critical velocity, v_c, given by equation (2.6). The miminum jetting velocity, v_j, was predicted by using equation (2.4) suggested by Ruff et al. (1976) and Ruff (1978).

Multiple regression analyses to find the constants $C_{4.1}$ and indices $m_{4.1}$ and $m_{4.2}$ gave the following correlations for the single drop and jetting regions :

$$\frac{\phi_{32}}{d} = 1.591\left(\frac{\Delta\rho d v^2}{\sigma}\right)^{-0.068}\left(\frac{\Delta\rho d^2 g}{\sigma}\right)^{-0.278} \qquad (4.2a)$$

for $0 < v < v_j$, and

$$\frac{\phi_{32}}{d} = 1.546\left(\frac{\Delta\rho d v^2}{\sigma}\right)^{-0.021}\left(\frac{\Delta\rho d^2 g}{\sigma}\right)^{-0.214} \qquad (4.2b)$$

for $v_j < v < v_c$

The average percentage deviation,

$$\gamma = \frac{100}{J}\sum_{i=1}^{J}\left|Q_n(\text{exp}) - Q_n(\text{pred})\right| / Q_n(\text{exp}) \qquad (4.3)$$

is given in Tables 4.2a and 4.2b for each of the data sources investigated. In this equation Q_n(exp) is the experimentally measured value and Q_n(pred) the predicted value. The average value of γ in the single drop region is 8.7 and in the jetting region 10.8%. These tables also list the values of γ for the other pertinent correlations available in the literature. Only in the single drop region do the other correlations approach the accuracy of equations (4.2a) and (4.2b). It is clear that Vediayan's (1969) correlation only applies to his own data, particularly in the single drop region. The terminal velocity in de Chazal and Ryan's (1971) correlation was calculated from Hu and Kintner's (1955) relationship. Almost identical values were obtained by using Klee and Treybal's (1956) relationship.

Table 4.2a Comparison of Different Correlations for the Prediction of Drop Diameter in Single Drop Region in Terms of Average Percentage Deviation, γ

Source	No.of data points	Scheele and Meister (1968a)	de Chazal and Ryan (1971)	Izard (1972)	Kagan et al. (1973)	Vedaiyan (1969)	Equation (4.2a)
Horvath (1976)	60	20.0	3.5	19.4	5.0	82.7	8.2
Vedaiyan (1969)	41	19.3	22.0	12.8	18.8	8.4	16.0
	9	12.5	14.9	12.4	14.6	6.6	13.8
	30	10.1	14.7	14.2	15.5	13.3	11.0
	34	13.1	14.0	5.2	6.6	5.4	6.6
Garwin and Smith (1969)	53	10.6	2.9	3.5	5.9	19.3	3.9
Loutaty et al. (1969)	6	21.0	10.2	17.5	12.4	63.7	4.0
Kumar and Hartland (1982)	6	22.0	9.4	24.4	6.9	106.0	4.6
	4	14.1	2.6	10.6	2.3	44.5	5.2
Totals or Means	243	15.3	10.1	11.9	9.6	33.6	8.7

Table 4.2b Comparisons of Different Correlations for the Prediction of Drop Diameter in Jetting Region in Terms of Average Percentage Deviation, γ

Source	No.of data points	Horvath et al. (1978)	Vedaiyan (1969)	Equation (4.2b)
Horvath (1976)	44	12.8	151.0	9.5
Vedaiyan (1969)	44	19.0	9.5	15.4
	11	20.4	3.2	14.3
	26	21.7	17.2	12.5
	16	22.0	4.4	7.9
Garwin and Smith (1953)	12	7.2	29.5	4.9
Loutaty et al. (1969)	40	25.9	82.3	9.0
Henton (1967)	4	18.0	16.2	6.3
Miller and Pilhofer (1976)	13	9.6	140.8	15.1
Bühler (1977)	22	15.9	12.8	6.6
Kumar and Hartland (1982)	4	13.9	228.7	20.9
	5	15.4	54.5	4.9
Totals or Means	241	18.0	60.7	10.8

Fifteen data points of Miller and Pilhofer (1976) which lie in the single drop region were not included in the analysis because perforated plates with a large number of holes (195 to 5910) were used and therefore one can not be sure that all the holes were operating at low dispersed phase flow rates. For these data points the diameters predicted by equation (4.2a) in the single drop region are consequently found to be significantly bigger than the experimental diameters. Similarly, Bühler's (1977) data in the single drop region are also not included, because his nozzle diameters were large (5 mm and 3 mm), so once again, one can not be certain that all the nozzles were operating when low flow rates were used.

Three data sources (Vedaiyan, 1969, Miller and Pilhofer, 1976, Loutaty et al., 1969) give drop sizes above the critical velocity; the first indicates a decrease in the drop size with nozzle velocity, the second an increase and the third furnishes only one data point. At the present time it is therefore not possible to predict the drop sizes in this range with any degree of certainty.

4.1.2 General Correlation

The variation of drop size with the nozzle velocity has been observed to be S-shaped (Garwin and Smith, 1953, Loutaty et al., 1969, Perrut and Loutaty, 1972, Horvath, 1976, Miller and Pilhofer, 1976) since in the single drop region the drop size decreases slowly with the increase of nozzle velocity; in the jetting region the drop size decreases exponentially with the nozzle velocity and is minimum at the critical velocity.

Horvath et al. (1978) formulated a correlation (equation (2.11)) for o-xylene/water system which predicts an exponential decrease of the drop size with the nozzle velocity in the jetting region. Although a logarithmic function of the type represented by equation (2.11) is well suited for the jetting region, such a function can not be extended to the single drop region since it could yield highly exaggerated values of the drop size in such regions.

Equation (2.11) has been modified below to include all the data sources listed in Table 4.2b. The analysis was simplified using equation (2.6) for the calculation of critical velocity whereas equations (2.7b,c) defining the critical drop diameter were retained. For 241 data points on 12 liquid/liquid systems the following equation was developed for the jetting region :

$$\frac{\phi_{32}}{\phi_c} = 3.83\left(\frac{\sigma}{\rho_d d v^2}\right)^{1/2} + 1.63 \log_e\left\{0.34\left(\frac{\rho_d d v^2}{\sigma}\right)^{1/2}\right\} \qquad (4.4)$$

This equation predicts the drop size with an average deviation of 8.5%.

A general correlation for the entire range of nozzle velocities may be expressed by the following functional relationship :

$$\frac{\phi_{32}}{d} = f(Fr,\ E\ddot{o},\ \Delta\rho/\rho_c) \qquad (4.5)$$

where Fr $(= v^2/g/d)$ is the nozzle Froude number. The values of Fr for the 12 liquid/liquid systems investigated are given in Table 4.1. The entire Fr range covered here was best fitted by a "logistic" equation as :

$$\frac{\phi_{32}}{d} = E\ddot{o}^{-0.38}\left\{1.63\left(\frac{\Delta\rho}{\rho_c}\right)^{0.41} + \exp(-0.16Fr)\right\} \qquad (4.6)$$

The parameters of equation (4.6) were computed using Marquardt's algorithim for least-squares estimation of non-linear parameters, the standard deviation in ϕ_{32}/d being 0.28.

Figure 4.1 shows the data of Horvath (1976) for o-xylene/water system together with the variation of ϕ_{32} with v predicted by equation (4.6). It can be seen that equation (4.6) predicts an S-shaped variation of the drop size with the nozzle velocity. Alternatively this equation predicts an exponential decrease of dimensionless drop diameter, ϕ_{32}/d, with the nozzle Froude number, Fr, as shown in Figure 4.2. Table 4.3a compares equations (4.2a,b), (4.4) and (4.6) in the single drop and jetting regions in terms of average percentage deviation, γ. Overall comparison of equations (4.2a,b) and (4.6) for the entire range of nozzle velocities is given in Table 4.3b. It can be

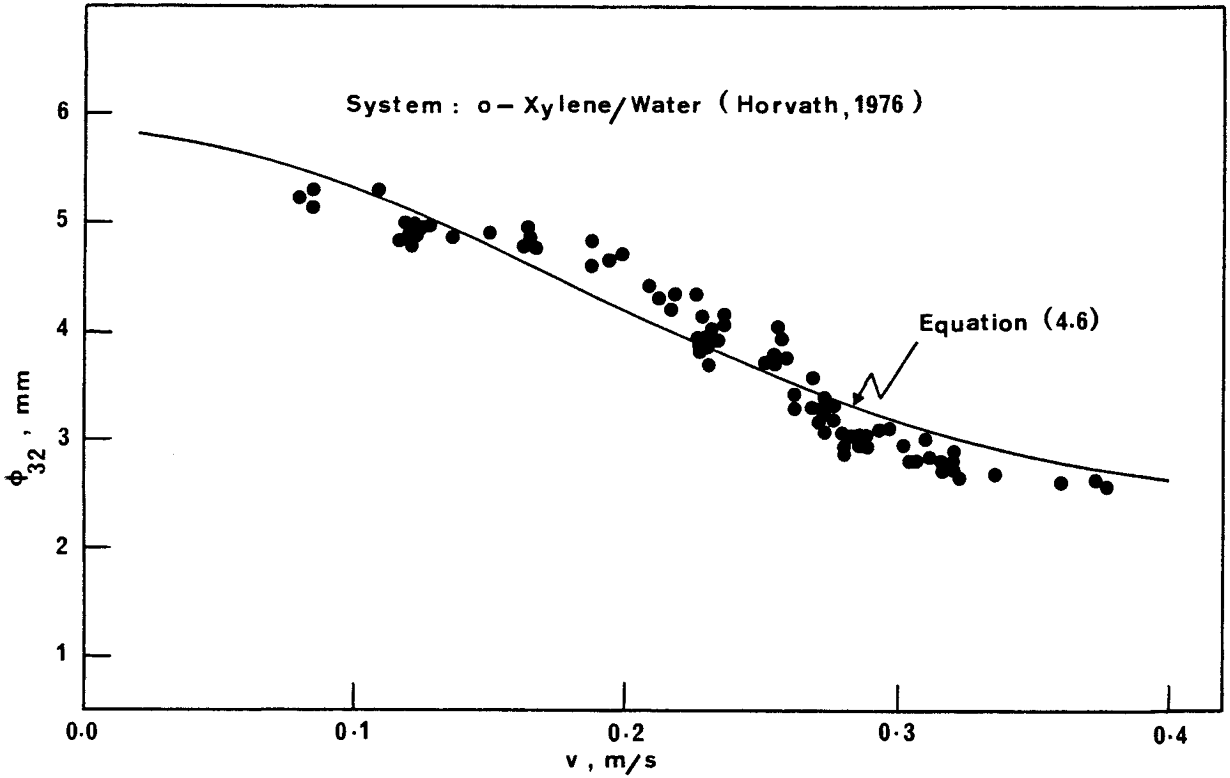


Figure 4.1 Variation of Drop Diameter, ϕ_{32}, with Nozzle Velocity, v

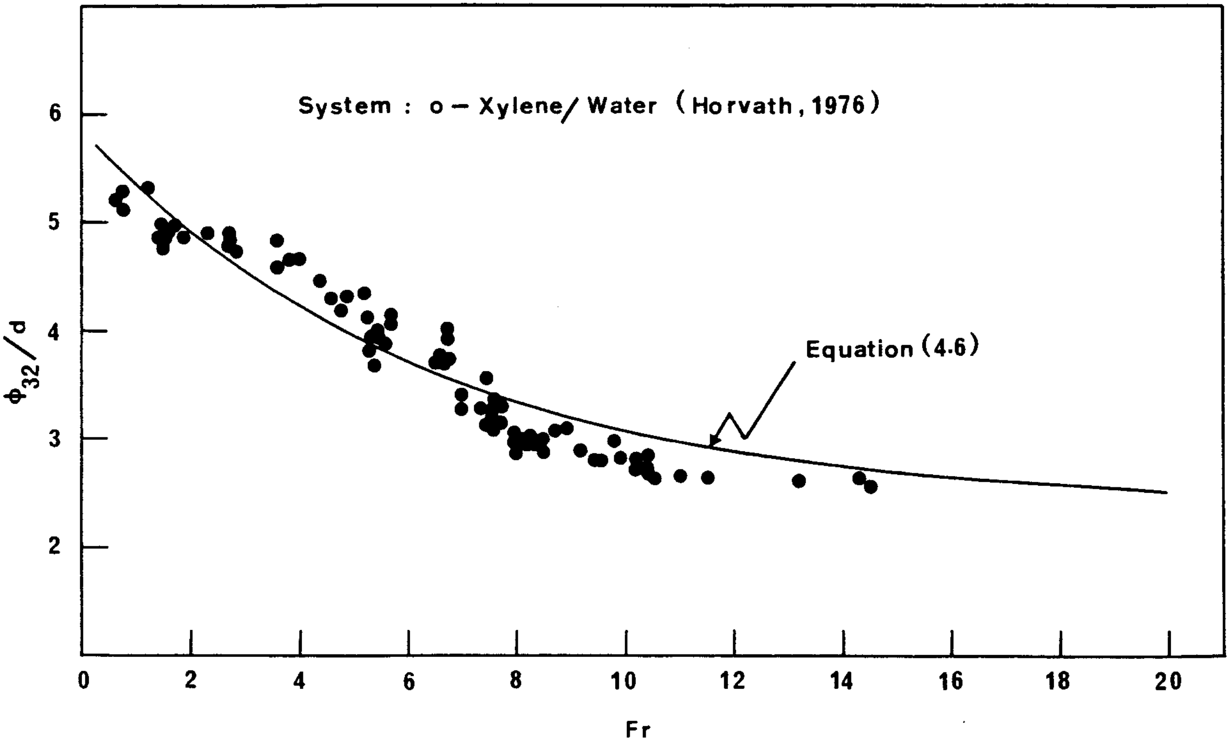


Figure 4.2 Variation of Dimensionless Drop Diameter, ϕ_{32}/d, with Nozzle Froude Number, Fr

Table 4.3a Comparison of Equations (4.2a,b), (4.4) and (4.6) for the Prediction of Drop Diameter in Single Drop and Jetting Regions in Terms of Average Percentage Deviation, γ

Source	Single Drop Region			Jetting Region			
	No.of data points	Equation (4.2a)	Equation (4.6)	No.of data points	Equation (4.2b)	Equation (4.4)	Equation (4.6)
Horvath (1976)	60	8.2	4.4	44	9.5	3.6	8.7
Vedaiyan (1969)	41	16.0	11.8	44	15.4	7.7	10.5
	9	13.8	13.5	11	14.3	5.8	9.0
	30	11.0	15.2	26	12.5	7.4	8.4
	34	6.6	15.0	16	7.9	7.9	9.6
Garwin and Smith (1953)	53	3.9	3.8	12	4.9	20.0	10.1
Loutaty et al.(1969)	6	4.0	13.3	40	9.0	9.5	10.6
Henton (1967)	-	-	-	4	6.3	14.4	13.3
Miller and Pilhofer (1976)	-	-	-	13	15.1	7.3	14.5
Bühler (1977)	-	-	-	22	6.6	14.7	7.3
Kumar and Hartland (1982)	6	4.6	9.7	4	20.9	12.8	20.1
	4	5.2	16.3	5	4.9	3.0	8.4
Totals or Means	243	8.2	9.2	241	10.8	8.5	9.9

Table 4.3b Comparison of Equations (4.2a,b) and (4.6) for the Prediction of Drop Diameter for the Entire Range of Nozzle Velocities in Terms of Average Percentage Deviation, γ

Source	No. of data points	Equations (4.2a,b)	Equation (4.6)
Horvath (1976)	104	8.8	6.2
Vedaiyan (1969)	85	15.7	11.1
	20	14.1	11.0
	56	11.7	12.0
	50	7.0	13.3
Garwin and Smith (1953)	65	4.1	5.0
Loutaty et al. (1969)	46	8.3	10.9
Henton (1967)	4	6.3	13.3
Miller and Pilhofer (1976)	13	15.1	14.5
Bühler (1977)	22	6.6	7.3
Kumar and Hartland (1982)	10	11.1	13.9
	9	5.0	11.9
Totals or Means	484	9.7	9.5

seen that correlation given by equation (4.6) predicts results of comparable accuracy to that given by equations (4.2a,b) and at the same time is simple to handle because of the absence of a break-point.

4.2 Correlation for Slip Velocity in Spray Columns

The correlation between slip velocity and drop diameter developed by Barnea and Mizrahi (1975e) may be improved by redefining the drag coefficient as :

$$C_{D\varepsilon,3} = \frac{4\Delta\rho g\phi_{32}}{3\ \rho_c V_s^2} \left(\frac{1-\varepsilon}{1+\varepsilon^{1/3}}\right)^{m_{4.3}} \qquad (4.7)$$

The introduction of index $m_{4.3}$ is expected to improve allowance for wall effects and drop distortion at high Reynolds numbers and hold-ups. The relationship between slip velocity and drop diameter may then be written as :

$$(Re_{\varepsilon,1}/C_{D\varepsilon,3})^{1/3} = C_{4.2}\{(C_{D\varepsilon,3}Re^2_{\varepsilon,1})^{1/3}\}^{m_{4.4}} \qquad (4.8)$$

In view of the difficulty in estimating the effective viscosity of the dispersed phase, μ_d^*, in equation (2.41a), the equation of Leviton and Leighton (1936) :

$$\frac{\mu_\varepsilon}{\mu_c} = \exp\{2.5\left(\frac{0.4 + \mu_d/\mu_c}{1 + \mu_d/\mu_c}\right)(\varepsilon + \varepsilon^{5/3} + \varepsilon^{11/3})\} \qquad (4.9)$$

was used to estimate the dispersion viscosity μ_ε. (As will be shown below,the definition of μ_ε is not important.) These values were used to calculate $Re_{\varepsilon,1}$ for 602 data points from nine different data sources listed in Table 4.4a, which gives the physical properties of 17 liquid/liquid systems. The operating conditions summarized in Table 4.4b show that for system 17 the range of Reynolds numbers (0.04 -0.26) is much less than for the other systems (7 -2450). The unknown constants in equations (4.7) and (4.8) were therefore determined using a multiple linear regression analysis using the data on the first 16 systems. The values of the indices $m_{4.3}$ and $m_{4.4}$ were 1.844 and 0.497 and the constant $C_{4.2}$ was 1.449. If μ_ε is replaced by μ_c the values become $m_{4.3}$ = 1.822 and $m_{4.4}$ = 0.510 and $C_{4.2}$ = 1.374. By approximating $m_{m.4}$ as 0.5

Table 4.4a Physical Properties of the Systems Investigated

Source	No. of data points	Phases		ρ_d kg/m^3	ρ_c kg/m^3	μ_d mPa s	μ_c mPa s	σ mN/m
		Dispersed	Continuous					
Bühler (1977)	199	Spindle oil	Water	786.2-804.8	980.6-995.2	1.1150-1.7030	0.7040-0.9040	24.6-29.5
Ferrarini (1972)	50	Spindle oil	Water	787.6-803.4	982.1-993.2	1.1440-1.6600	0.7160-0.8520	25.9-26.6
Loutaty et al. (1969)	52	Kerosene	Water	780.7-805.7	986.4-993.0	0.7670-1.0780	0.7590-0.8550	44.5
Horvath (1976)	104	o-Xylene	Water	880.2	998.96	0.81	1.00	30.7
Weaver (1958)	10	Methylisobutylketone	Water	799.5	997.1	0.8252	0.8937	8.82
	14	Isobutanol	Water	818.5	997.1	4.2789	0.8937	2.08
	6	Toluene	Water	859.5	997.1	0.7158	0.8937	30.3
	5	Isoamylalcohol	Water	822.0	997.1	4.8812	0.8937	4.58
Maraschino and Treybal (1971)	2	Benzene	Water	875.0-875.4	997.7-998.0	0.613-0.626	0.948-0.957	29.1-32.1
	1	Cyclohexane	Water	773.5	997.0	0.860	0.874	47.8
	2	n-Butylacetate	Water	880.2-880.5	998.4-998.5	0.711-0.764	0.967-0.976	13.4-13.5
	2	Methylisobutylketone	Water	803.5	996.0	0.596	1.015-1.016	10.0-10.05
	2	Diisobutylcarbinol	Water	808.2	996.4	8.45-8.47	0.862	16.8-16.9
	1	1,2,3,6-Tetrahydrobenzaldehyde	Water	975.6	999.8	1.989	1.096	12.6

Table 4.4a (Continued)

Source	No. of data points	Phases		ρ_d kg/m^3	ρ_c kg/m^3	μ_d mPa s	μ_c mPa s	σ mN/m
		Dispersed	Continuous					
Hazlebeck and Geankoplis (1963)	16	Methylisobutyl-ketone	Water	800.6	995.0	0.576	0.933	10.7
Henton (1967)	125	Methyisobutyl-ketone	Water	799.5	997.1	0.8252	0.8937	8.82
Barnea and Mizrahi (1975e)	11	Brine	Butanol	1280.0-1287.0	881.0-886.0	5.33-6.62	5.79-8.35	4.9-6.2

Table 4.4b Range of Operating Conditions

Source	Phases Dispersed	Phases Continuous	ε	ϕ_{32} mm	$Re_{\varepsilon,1}$	$C_{D\varepsilon,3}$	$\frac{V_s^2}{\phi_{32}g}$	$\frac{\Delta\rho}{\rho_c}$	$\frac{(1-\varepsilon)}{(1+\varepsilon^{1/3})}$
Bühler (1977)	Spindle oil	Water	0.0094-0.4931	2.99-9.09	38-2450	0.230-0.788	0.073-0.849	0.1913-0.1982	0.2832-0.8180
Ferrarini (1972)	Spindle oil	Water	0.035-0.248	5.26-8.79	528-1037	0.264-0.719	0.109-0.580	0.1911-0.1980	0.4618-0.7272
Loutaty et al. (1969)	Kerosene	Water	0.024-0.750	3.09-4.69	7-725	0.308-0.601	0.021-0.354	0.1886-0.2085	0.1310-0.7575
Horvath (1976)	o-Xylene	Water	0.0097-0.2033	2.56-5.28	69-894	0.183-0.769	0.060-0.576	0.1189	0.5017-0.8162
Weaver (1958)	Methylisobutylketone	Water	0.04-0.24	2.02-3.42	63-375	0.379-0.516	0.128-0.335	0.1982	0.4687-0.7154
	Isobutanol	Water	0.04-0.28	1.34-1.78	17-112	0.568-0.969	0.054-0.227	0.1791	0.4353-0.7154
	Toluene	Water	0.04-0.24	2.90-3.35	128-317	0.341-0.439	0.111-0.292	0.1380	0.4687-0.7154
	Isoamylalcohol	Water	0.04-0.20	2.38-2.62	92-206	0.466-0.505	0.133-0.272	0.1756	0.5048-0.7154
Maraschino and Treybal (1971)	Benzene	Water	0.0328-0.0373	3.34-3.55	226-254	0.595-0.640	0.144-0.152	0.1226-0.1233	0.7216-0.7327
	Cyclohexane	Water	0.0373	3.12	343	0.468	0.351	0.2242	0.7216
	n-Butylacetate	Water	0.0298-0.0582	2.61-2.67	148-187	0.466-0.514	0.151-0.195	0.1182-0.1184	0.6788-0.7406
	Methylisobutylketone	Water	0.0236-0.0472	1.98-2.01	128-159	0.437-0.503	0.266-0.355	0.1933	0.6999-0.7588

Table 4.4b (Continued)

Source	Phases Dispersed	Continuous	ε	ϕ_{32} mm	$Re_{\varepsilon,1}$	$C_{D\varepsilon,3}$	$\frac{V_s^2}{\phi_{32}g}$	$\frac{\Delta\rho}{\rho c}$	$\frac{(1-\varepsilon)}{(1+\varepsilon^{1/3})}$
Maraschino and Treybal (1971)	Diisobutylcarbinol	Water	0.0302- 0.0598	2.44	159- 197	0.608- 0.665	0.185- 0.238	0.1889	0.6759- 0.7395
	1,2,3,6-Tetrahydrobenzaldehyde	Water	0.0647	4.46	94	0.937	0.016	0.0242	0.6674
Hazlebeck and Geankoplis (1963)	Methylisobutylketone	Water	0.0154- 0.0461	3.4	294- 367	0.463- 0.768	0.211- 0.323	0.1954	0.7021- 0.7884
Henton (1967)	Methylisobutylketone	Water	0.020- 0.172	2.41- 3.94	124- 525	0.277- 0.634	0.165- 0.561	0.1982	0.5321- 0.7708
Barnea and Mizrahi (1975e)	Brine	Butanol	0.215- 0.604	0.517- 1.040	0.04- 0.26	30.6- 102.5	0.0005- 0.0044	0.4526- 0.4529	0.2146- 0.4909

Table 4.5a Prediction of Dispersed Hold-up and Slip Velocity by Using Equation (4.10) in Terms of Average Percentage Deviation, γ

Source	No. of data points	Hold-up	Slip Velocity
Bühler (1977)	199	11.4	8.3
Ferrarini (1972)	50	11.8	12.0
Loutaty et al. (1969)	52	10.6	6.8
Horvath (1976)	104	17.3	14.6
Weaver (1959)	10	8.0	7.2
	14	25.6	36.9
	6	13.7	11.9
	5	1.7	1.7
Hazlebeck and Geankoplis (1963)	16	6.4	7.1
Henton (1967)	125	8.5	7.7
Totals or Means	581	11.9	10.1

the values of $m_{4.3}$ and $C_{4.2}$ giving the best fit are 1.834 and 1.430, and the Reynolds number disappears from equation (4.8) which then becomes :

$$\frac{V_s^2}{\phi_{32}g} = 2.725\,\frac{\Delta\rho}{\rho_c}\left(\frac{1-\varepsilon}{1+\varepsilon^{1/3}}\right)^{1.834} \qquad (4.10)$$

Thus the value of $C_{D\varepsilon,3}$ is constant and equal to 0.49.

Equations (2.29) and (4.10) were solved for ε numerically, minimizing the absolute value of the difference in V_s^2 for

Table 4.5b Comparison of Different Correlations for the Prediction of Slip Velocity in Terms of Average Percentage Deviation, γ

Source	No. of data points	Pilhofer (1974)	Barnea and Mizrahi (1975e)	Equation (4.10)
Bühler (1977)	199	15.1	21.6	6.9
Ferrarini (1972)	50	16.6	45.2	8.5
Loutaty et al. (1969)	52	12.4	19.2	7.7
Horvath (1976)	104	18.4	8.6	11.6
Weaver (1959)	10	6.2	5.9	5.6
	14	6.6	11.0	24.8
	6	3.3	4.7	8.9
	5	5.4	7.6	1.3
Maraschino and Treybal (1971)	10	25.0	11.1	10.5
Hazlebeck and Geankoplis (1963)	16	44.5	12.6	6.4
Henton (1967)	125	11.6	12.5	6.4
Total or Means	591	15.2	17.9	8.2

the data sources listed in Table 4.5a (6 liquid/liquid systems investigated by Maraschino and Treybal (1971) are not included in this table since the phase flow rates are not mentioned in the original reference). This was done by using a modified Newton's method for the solution of a single non-linear equation. However, the computations were found to be sensitive to any error in the flow rates and the solution to about 8% of the total number of data points listed in Table 4.5a was obtained by using a direct search method. Predicted values of hold-up were in turn used to calculate slip velocities. Table 4.5a compares the experimental and predicted hold-up and slip velocity values in terms of average percentage deviation, γ. The average values of γ are 11.9% and 10.1% for the hold-up and slip velocity respectively. It can also be seen that equation (4.10) gives good estimates for hold-up and slip velocity for all systems but one. Predicted hold-ups for 14 data points on isobutanol/water system investigated by Weaver (1959) were found to be consistently lower than the experimental values. It is difficult to offer any satisfactory explanation at this stage. The correlation given by equation (4.10) may possibly be improved by adding to it a dimensionless group containing interfacial tension.

Equation (4.10) has also been assessed with regard to two other pertinent correlations available in the literature by comparing the experimental and predicted slip velocities. Table 4.5b compares the slip velocity values predicted by the correlations of Pilhofer (1974) and Barnea and Mizrahi (1975e) discussed in Section 2.3.2 and equation (4.10) in terms of average percentage deviation, γ. In view of the rather tedious trial-and-error computation involved in the calculation of hold-up, slip velocity values for these three correlations were calculated by using experimental hold-ups. The average value of γ for the correlations of Pilhofer and Barnea and Mizrahi are 15.2% and 17.9% respectively, whereas that for equation (4.10) is only 8.2%.

Since the computation of hold-up is normally difficult, Figures 4.3 and 4.4 have been prepared, eliminating the necessity of trial-and-error solution for ε and V_s. It could be seen from these figures that two values of hold-up (or slip velocity) are possible with each pair of flow rates. It has been shown experimentally (Letan and Kehat, 1967, Loutaty and Vignes, 1969, Loutaty et al., 1969, Lackme, 1974) that each of the two solutions has a physical meaning corresponding to loose and dense-packed dispersions respectively. More about these two regimes of operation in a spray column has been given by Lackme (1974), Steiner et al. (1978) and Steiner and Hartland (1983).

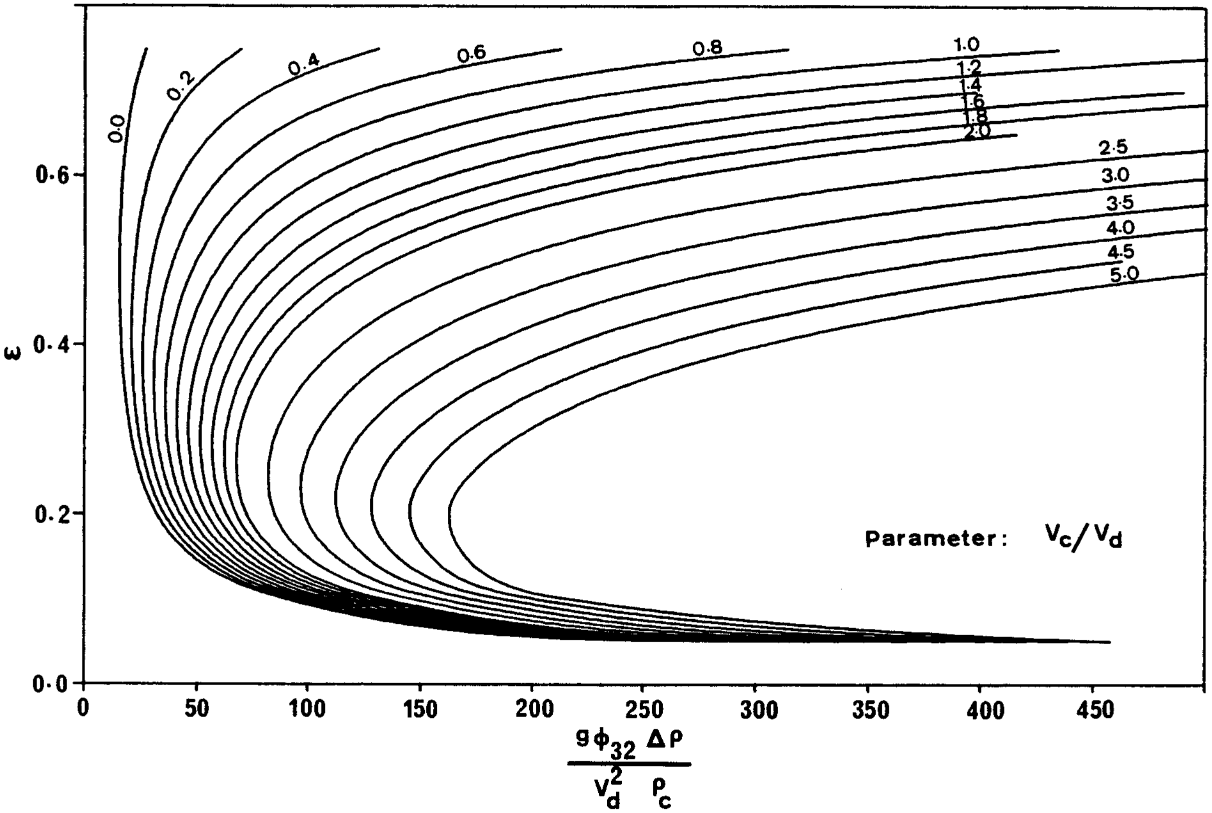


Figure 4.3 Graphical Solution of Equation (4.10)

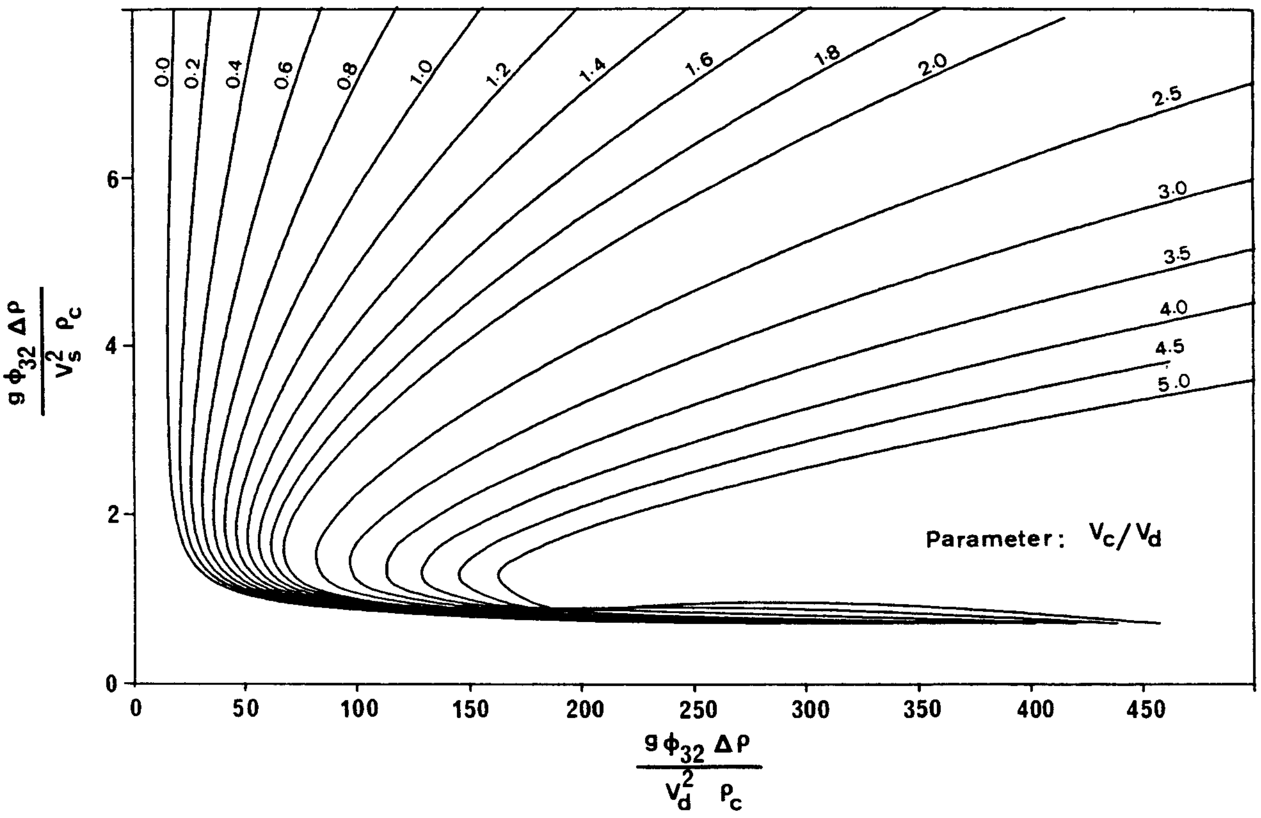


Figure 4.4 Graphical Solution of Equation (4.10)

4.3 Correlations for Dispersed Phase Hold-up in Pulsed Sieve-Plate Columns

Only a qualitative description of different flow regimes in pulsed sieve-plate extraction columns was given in Section 2.3.3. Before the dependence of hold-up on the column geometry, operating variables and physical properties of the phases can be expressed in dimensionless form as a product of dimensionless groups and the relevant indices obtained, it is necessary to determine the break-points between mixer-settler and dispersion regions and dispersion and emulsion regions of operation. Based on the data of Sehmel (1961) on 3 liquid/liquid systems, Sehmel and Babb (1963) presented a correlation for the transition point between mixer-settler and dispersion-type operation which was the frequency for minimum hold-up :

$$f = 0.667\ (-3.373 + 3.883 \times 10^2 \mu_d\ \sigma \Delta\rho - \ln A) \qquad (4.11)$$

The quantities in this equation are in SI units. (In the original reference mixed units were used, namely, feet, inches, pounds, hours and minutes; moreover, the constants were incorrectly quoted).

Bell and Babb (1969) found that all the data for a given system exhibited a minimum hold-up at the same Af value. Although these authors employed the same liquid/liquid systems (n-hexane/water and methyl isobutyl ketone/water) and a similar column to that used by Sehmel (1961), the values predicted by equation (4.11) do not correspond to the required value of the Af product for minimum hold-up for their data. Other criteria have also been defined (Sato et al., 1963, Maksimenko et al., 1966), the first being relevant to the particular liquid/liquid system and the second applying to reciprocating-plate columns.

Table 4.6a gives the physical properties for 1103 data points for 10 liquid/liquid systems in which the solvent was dispersed and no mass transfer occurred, taken from 7 different data sources. The operating conditions and column dimensions are summarized in Table 4.6b. The last two data sources were not included in the analysis for the reasons given later in this section. Equation (4.11) was used to separate the data points

Table 4.6 a Physical Properties of Systems Investigated

Source	No. of data points	Phases Dispersed	Phases Continuous	ρ_d kg/m^3	ρ_c kg/m^3	μ_d mPa s	μ_c mPa s	σ mN/m
Mishra and Dutt (1969)	73	Toluene	Water	862.3	997.05	0.5520	0.8904	33.5
Toller (1981)	23	Toluene	Water	866.94	998.21	0.5870	1.00	35.7
Ugarcic (1981)	70	o-Xylene	Water	881.0	1000.00	0.81	1.00	30.7
Sehmel (1961)	117	Hexane	Water	651.96	996.38	0.2873	0.8420	38.745
	55	Benzene	Water	871.42	996.38	0.58	0.8420	32.13
	46	Methyl isobutyl-ketone	Water	796.13	996.38	0.5544	0.8420	10.325
Bell (1964)	201	Hexane	Water	659.97	998.00	0.2939	0.9779	46.55
	140	Methyl isobutyl-ketone	Water	807.34	998.00	0.4919	0.9979	10.22
Arthayukti (1975)	58	Carbontetra-chloride	Water	1590.00	1000.00	0.95	1.00	45.0
Niebuhr and Vogelpohl (1980), Niebuhr (1982a)	320	Toluene	Water	860.0	1000.00	0.57	1.00	35.0

Table 4.6b Operating Conditions and Column Dimensions

Source	ε	Af mm/s	V_d mm/s	V_c mm/s	T mm	ℓ mm	d_o mm	κ
Mishra and Dutt (1969)	0.0148- 0.0723	8.33- 30.26	0.89- 2.39	1.42- 2.42	76.2	50.0, 100.0	4.76, 6.35	0.226, 0.36
Toller (1981)	0.0130- 0.1130	6.99- 19.00	1.39- 3.61	1.39- 3.61	47.3	100.0	2.0	0.20
Ugarcic (1981)	0.0110- 0.1010	9.80- 31.65	1.37- 4.29	1.27- 6.66	101.5	100.0	2.0	0.224
Sehmel (1961)	0.0120- 0.2530	2.14- 63.50	1.74- 4.34	0.00- 4.34	50.0	50.3	3.175	0.23
	0.0270- 0.3830	3.18- 39.53	1.74- 4.34	1.74- 4.34	50.0	50.3	3.175	0.23
	0.0340- 0.1780	2.07- 36.83	1.74- 4.34	1.74- 4.34	50.0	50.3	3.175	0.23
Bell (1964)	0.0107- 0.6330	3.59- 88.66	1.23- 5.76	0.00- 5.32	50.8	55.9	3.175	0.23
	0.0128- 0.5700	4.27- 84.67	1.16- 4.74	0.00- 5.38	50.8	55.9	3.175	0.23
Arthayukti (1975)	0.0064- 0.1256	29.25- 89.53	0.14- 0.50	5.66	50.0	50.0	2.0	0.20
Niebuhr and Vogelpohl (1980), Niebuhr (1982a)	0.0047- 0.6259	7.42- 21.67	0.38- 9.78	0.37- 10.85	72.0, 213.0	50.0	2.0	0.20

in the mixer-settler region for Sehmel's (1961) results and the reported Af products for the minimum hold-up (Bell and Babb, 1969) for Bell's (1964) data.

The break-point between dispersion and emulsion regions of operation was determined in the following manner: Equation (2.45), defining the rate of energy dissipation per unit mass of the mixed phases, was made dimensionless :

$$E = \frac{(Af)^3}{\lambda \ell} \cdot \frac{\rho_c}{\Delta\rho^{3/4}\,\sigma^{1/4}\,g^{5/4}} \qquad (4.12)$$

and used as a criterion to separate the two regions.

Based on the data in Tables 4.6a and 4.6b the following correlations were developed with a break-point at E = 0.05.
For the dispersion region $(E < 0.05)$:

$$\varepsilon = 6.91 \left\{\frac{(Af)^3 \rho_c^{1/4}}{\lambda \ell \sigma^{1/4} g^{5/4}}\right\}^{0.31} \left(\frac{V_d^4 \rho_c}{g\ \sigma}\right)^{0.30} \left(1 + \frac{V_c}{V_d}\right)^{0.14} \cdot \left(\frac{\Delta\rho}{\rho_c}\right)^{-0.79} \left(\frac{\mu_d^4\ g}{\rho_c \sigma^3}\right)^{-0.01} \qquad (4.13a)$$

For the emulsion region $(E > 0.05)$:

$$\varepsilon = 3.73\times10^{-3} \left\{\frac{(Af)^4 \rho_c}{g\ \sigma}\right\}^{0.62} \left(\frac{V_d^4 \rho_c}{g\ \sigma}\right)^{0.31} \left(1 + \frac{V_c}{V_d}\right)^{0.45} \cdot \left(\frac{\Delta\rho}{\rho_c}\right)^{-2.20} \left(\frac{\mu_d^4\ g}{\rho_c \sigma^3}\right)^{-0.29} \qquad (4.13b)$$

Equation (4.13a) is based on 367 data points for 8 systems and equation (4.13b) on 151 data points for 4 systems, listed in Table 4.7a. The hole diameter was not considered as a variable since it was about 3 mm for most of the data points. In addition, for the two data sources (Sehmel, 1961, Bell, 1964) investigated in the emulsion region, the plate free area was held constand and place spacing did not alter much, so were not included in equation (4.13b).

Consideration of 207 data points for 5 liquid/liquid systems from two data sources (Sehmel, 1961, Bell, 1964) gave the following correlation for the mixer-settler region :

$$\varepsilon = 3.91\text{x}10^{-3}\left(\frac{A^2\rho_c g}{\sigma}\right)^{-0.26}\left(\frac{f^4\sigma}{\rho_c g^3}\right)^{-0.19}\left(\frac{V_d^4\ \rho_c}{g\ \sigma}\right)^{0.28} \cdot \left(1+\frac{V_c}{V_d}\right)^{0.19}\left(\frac{\Delta\rho}{\rho_c}\right)^{-0.81}\left(\frac{\mu_d^4 g}{\rho_c\sigma^3}\right)^{-0.13} \qquad (4.13c)$$

Hole size, plate free area and plate spacing were not included in the analysis for the reasons stated in the foregoing paragraph. Moreover, in equation (4.13c) A and f were treated as separate variables since this led to better agreement between experimental and predicted hold-up values than when A and f were combined.

This suggests that the rate of energy dissipation per unit mass of the mixed phases is not the controlling factor in the mixer-settler region of operation as in dispersion and emulsion regions. Equation (4.13c) should be used to predict the hold-up when $E < 0.05$ and the predicted value is greater than that predicted by equation (4.13a) for the dispersion region. The column diameter does not appear in any of the correlations. Rouyer et al.(1974) found that the operation of columns up to 600 mm diameter was not affected by the column diameter.

The average percentage deviation, γ, in hold-up is given in Table 4.7a for the mixer-settler, dispersion and emulsion regions for each of the data sources investigated. The average value of γ in the mixer-settler region is 13.5% and in the dispersion and emulsion regions 12.4 and 13.7% respectively.

The values of the hold-ups predicted by the proposed correlations for the dispersion and emulsion regions (equations (4.13a,b)) are compared with those predicted by the correlations of Miyauchi and Oya (1965) and Mishra and Dutt (1969) in Table 4.7b. Linear regressions were performed to calculate the relevant constant $C_{2.17}$ in the equation of Mishra and Dutt (see Table 2.4) for each system using experimental data points. Their correlation appears only to be applicable in the dispersion region, i.e. for moderate pulsation velocities

Table 4.7a Prediction of Hold-up in Mixer-Settler, Dispersion and Emulsion Regions in Terms of Average Percentage Deviation, γ

Source	Mixer-Settler Region		Dispersion Region		Emulsion Region	
	No. of data points	Equation (4.13c)	No.of data points	Equation (4.13a)	No. of data points	Equation (4.13b)
Mishra and Dutt (1969)	-	-	73	10.8	-	-
Toller (1981)	-	-	23	20.6	-	-
Ugarcic (1981)	-	-	70	10.2	-	-
Sehmel (1961)	66	12.1	46	16.1	5	17.1
	31	12.3	23	8.9	1	2.7
	15	14.1	31	14.2	-	-
Bell (1964)	68	15.2	50	9.9	83	15.3
	27	13.9	51	13.8	62	11.5
Totals or Means	207	13.5	367	12.4	151	13.7

Table 4.7b Comparison of Different Correlations for the Prediction of Hold-up in Dispersion and Emulsion Regions in Terms of Average Percentage Deviation, γ

Source	No.of data points	Miyauchi and Oya (1965)	Mishra and Dutt (1969)	Equations (4.13a,b)
Mishra and Dutt (1969)	73	14.6	4.2	10.8
Toller (1981)	23	24.5	36.0	20.6
Ugarcic (1981)	70	15.4	9.7	10.2
Sehmel (1961)	51	38.1	26.4	16.2
	24	21.0	32.5	8.6
	31	11.7	15.9	14.2
Bell (1969)	133	42.7	82.2	13.3
	113	43.4	41.7	12.5
Totals and Means	518	31.1	38.8	12.8

and throughputs. The average percentage deviations for these two correlations are 31% and 39% respectively, whereas that for equations (4.13a,b) is only 13%. No comparison is presented for the mixer-settler region since no other generalized correlation is available.

Figure 4.5 shows the experimental data of Bell (1964) for the methyl isobutyl ketone/water system with flow rates V_c=2.51 mm/s and V_d=2.39 mm/s, together with the variation of ε with Af predicted by equations (4.13a-c) for the dispersion, emulsion and mixer-settler regions respectively. Once again the agreement can be seen to be good.

58 data points of Arthayukti (1975) on carbontetrachloride/water system, which lie in the dispersion and emulsion regions of operation, were not included in the analysis since his data were obtained at very low dispersed phase flow rates (V_d = 0.14 to 0.50 mm/s) and extreme flow ratios ($11 < V_c/V_d < 40$). For these data points the hold-up values predicted by equations (4.13a,b) are found to be consistently lower than the experimental values. For such data with very low dispersed phase flow rates and extreme V_c/V_d ratios, equations (4.13a,b) can be fitted with the same indices on the dimensionless groups but to give different constants.

Niebuhr and Vogelpohl (1980) and Niebuhr (1982a) investigated toluene/water system with two different columns of diameter 72 mm and 213 mm and reported a total of 320 hold-up measurements. Based on 163 measurements on the first column, Niebuhr and Vogelpohl (1980) presented a correlation in cgs units, which has the same form as that given by Bell and Babb (1969):

$$\varepsilon = V_d\{0.215 + (3.4\times10^{-6} + 0.347V_c)(Af - 1.58)^2\} \qquad (4.14)$$

These authors claim that all the data points lie within ±20% of the above correlation. However, our calculations performed with the raw data supplied by Niebuhr (1982a) reveal that only 46% of the data points lie within ±20% of equation (4.14).

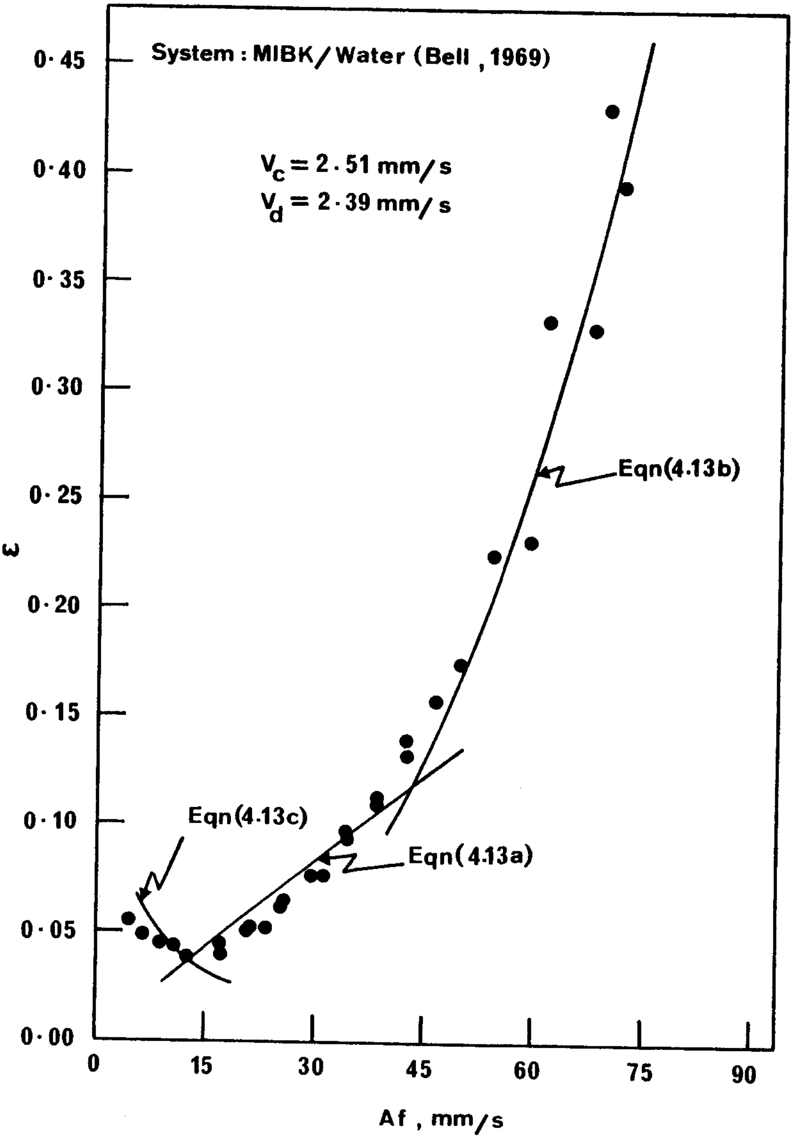


Figure 4.5 Variation of ε with Af Product for the System MIBK/Water with V_c = 2.51 mm/s and V_d = 2.39 mm/s (Black Dots) Measured by Bell (1964) and Predicted by Equations (4.13a-c) (Full Lines) for Dispersion, Emulsion and Mixer-Settler Regions

If the same equation, with the assumption that the column diameter does not affect column operation, is used to predict the hold-up values for 213 mm diameter column, the percentage of data points which lie within ±20% are 51.6.

Niebuhr (1982b) attributed the uncertainties in his data to the following :

1) temperature was not controlled and all the experiments were performed at room temperature;

2) some hold-up values were recorded when the column was operating near flooding point;

3) in some of the experiments the phase flow rates did not stablize.

For the reasons given above Niebuhr's data points were not included in the formulation of equations (4.13a,c) for the dispersion and mixer-settler regions (30% of his data points lie in the dispersion region and the remaining 70% in the mixer-settler region). Equations (4.13a,c) predict 320 data points of Niebuhr with an average deviation of 27.5% which is comparable to 27.2% given by the correlation of Niebuhr and Vogelpohl (1980) (Equation (4.14)).

5. EXPERIMENTAL WORK ON THE COALESCENCE OF LIQUID/LIQUID DISPERSIONS

The coalescence of liquid/liquid dispersions was investigated in two types of apparatus. A single-stage continuous mixer-settler was used to study the continuous settler characteristics, and the effects of mixing regime and phase ratio. Batch tests were also performed using the same mixing tank. The second apparatus used was a spray column since it provides some advantages over studies involving mechanical agitation, as pointed out earlier in Section 3.2.5. Moreover, the average drop size produced by a drop distributor in a spray column is an order of magnitude greater than that encountered in a mechanically agitated vessel.

5.1 Mixer-Settler Apparatus

A schematic diagram of the apparatus is shown in Figure 5.1. The mixing tank comprised a QVF glass column of 200 mm diameter and 300 mm high fitted with a dispersion exit port 15 mm in diameter at 90 degrees to the column wall and 200 mm above the base, and 10 mm thick stainless steel end-plates. Two 15 mm diameter holes in the bottom end-plate served as the light and heavy phase inlet ports. Four equally spaced vertical wall baffles,each 20 mm wide, made of stainless steel were welded to the top end-plate. A six-bladed flat-blade turbine 67 mm in diameter, attached to a stainless steel shaft, was located at 100 mm above the bottom of the mixing tank. The shaft was connected to a 120 W drive motor which provided a continuously variable output speed of 0 to 24 rps.

The dispersion overflowed by gravity into the settler which consisted of a glass QVF column, 100mm in diameter and 500 mm high, by means of a dispersion inlet port situated 90 degrees to the settler wall and 150 mm above the base of the settler. The separated phases overflowed into their respective storage tanks and were recirculated back into the mixing tank by means of two centrifugal pumps (QVF type GPB 3/30A) and two rotameters with fine control needle valves.

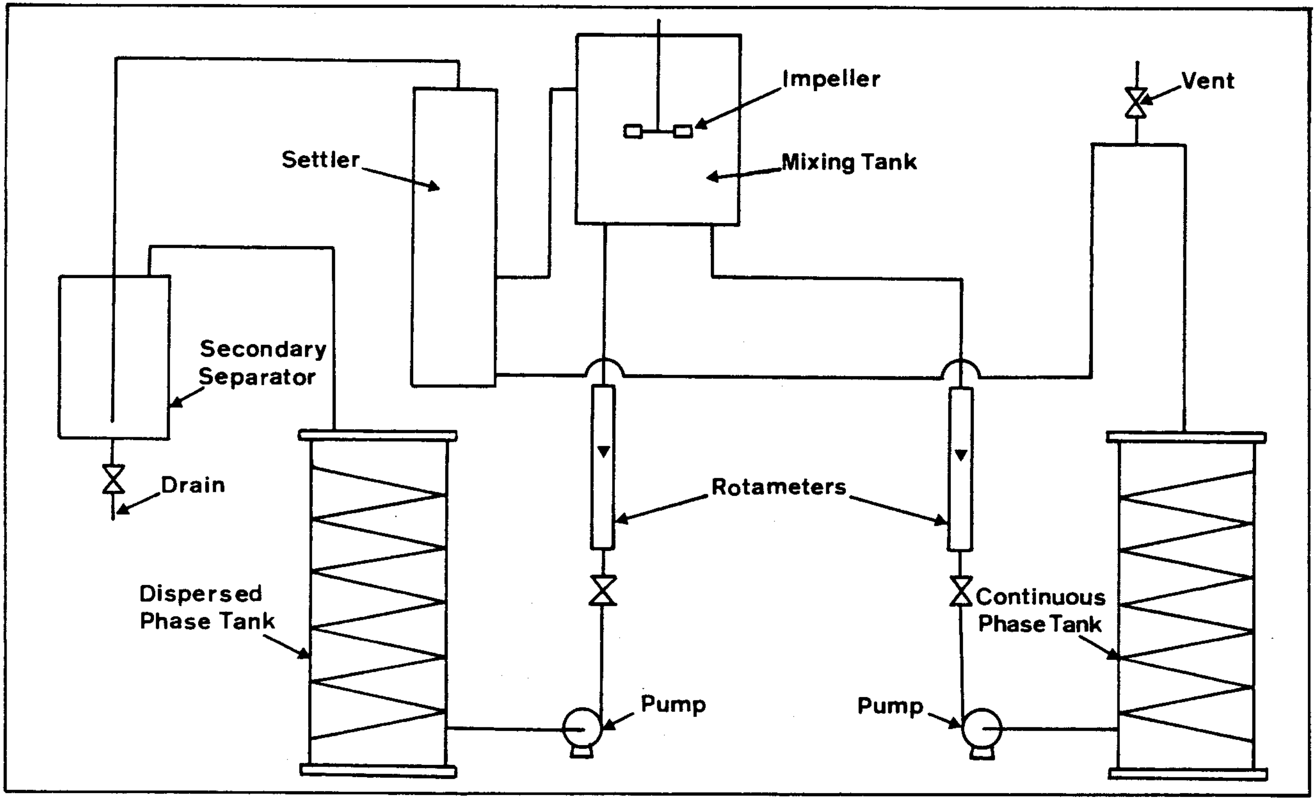


Figure 5.1 Schematic Diagram of Mixer-Settler Apparatus

5.1.1 Liquid/Liquid System and Experimental Procedure

A mixture of 40% paraffin oil and 60% toluene was selected as dispersed phase and deionized water as the continuous phase. The physical properties of mutually saturated phase at 20°C were ρ_d = 870.5 kg/m^3, ρ_c = 998.0 kg/m^3, μ_d = 1.64 mPa s, μ_c = 1.01 mPa s and σ = 38.0 mN/m. The densities were measured using a pyknometer, viscosities by an Ubbelhode viscometer and the interfacial tension by a drop volume method.

Before experimentation the apparatus was thoroughly cleaned first by rinsing with hot water, soaking in dilute nitric acid for 24 hours, draining, flushing with tap water, soaking in acetone for 24 hours, draining, then flushing twice with deionized water.

The storage tanks were then filled with the respective liquids, the thermostatic set-up switched on, pumps put into activation and the dispersed and continuous liquids placed in the mixer to give a phase ratio of 1 : 1.5. The supply of both the phases to the mixing tank was temporarily cut off by closing the needle valves and the agitator then started, the speed being set at 8 rps (complete mixing was observed at this speed). In this way the 40% paraffin oil + 60% toluene mixture was dispersed in water. After a few minutes mixing time the needle valves were re-opened, the ratio of dispersed to continuous liquids set at 1 : 1.5 and the liquids circulated for about 24 hours to ensure mutual saturation of the phases. An arbitrary value of 12 litre/hr of the dispersed phase was chosen for this purpose.

Five characteristics for continuous settler behaviour at the steady state were determined under different conditions. The parameters varied were the mixing speed and feed dispersion concentration (phase ratio).

A typical continuous experiment was performed by switching on the thermostatic set-up, starting the agitator and pumps and adjusting the throughput of each phase, measured by means of calibrated rotameters to give the desired phase ratio and total throughput. The liquids were circulated and the dispersion band height recorded every ten minutes. The steady state was considered to have been achieved when three successive readings of the dispersion height matched within ± 2 % (the average was used). More than one hour was generally needed to obtain each point on the settler's characteristics, two hours and ten minutes being the longest period observed.

A typical batch experiment was carried out, wherein the supply of both the liquids to the mixing tank was abruptly stopped; the agitator motor was then switched off and the dispersion allowed to collapse by sedimentation and coalescence processes. The levels of the sedimenting and coalescence fronts were recorded as a function of time. The movement of these fronts of the dispersion band was sufficiently slow to be observed visually.

5.1.2 Results

i) Continuous Settling - Effect of Mixing Intensity

The effect of mixing intensity on the continuous settler characteristics is shown in Figure 5.2a in terms of energy dissipation per unit mass group, N^3D^2. In these experiments the ratio of the dispersed to the continuous phase was kept at 1 : 1.5. It can be seen from the figure that the dispersion band height, H, increases with both the dispersed phase throughput per unit area, Q_d/R, and the mixing speed, N (curves A and B). Curve C ($N^3D^2 = 4.81\ m^2/s^3$) however, shows lower dispersion heights as compared with curve B ($N^3D^2 = 2.95\ m^2/s^3$) for Q_d/R more than 0.46 mm/s. This could be attributed to the fact that fresh continuous phase was used for this particular run and one would expect the fresh liquids to be free of surface active contaminants. But for Q_d/R less than 0.46 mm/s, the dispersion heights given by curve C are higher than those given by curves A and B. This may be due to the fact that the residence time of the dispersed phase in the mixing tank, which varied from 20 to 36 seconds for these runs, is higher at low dispersed phase throughputs and hence smaller drop sizes and higher dispersion band heights.

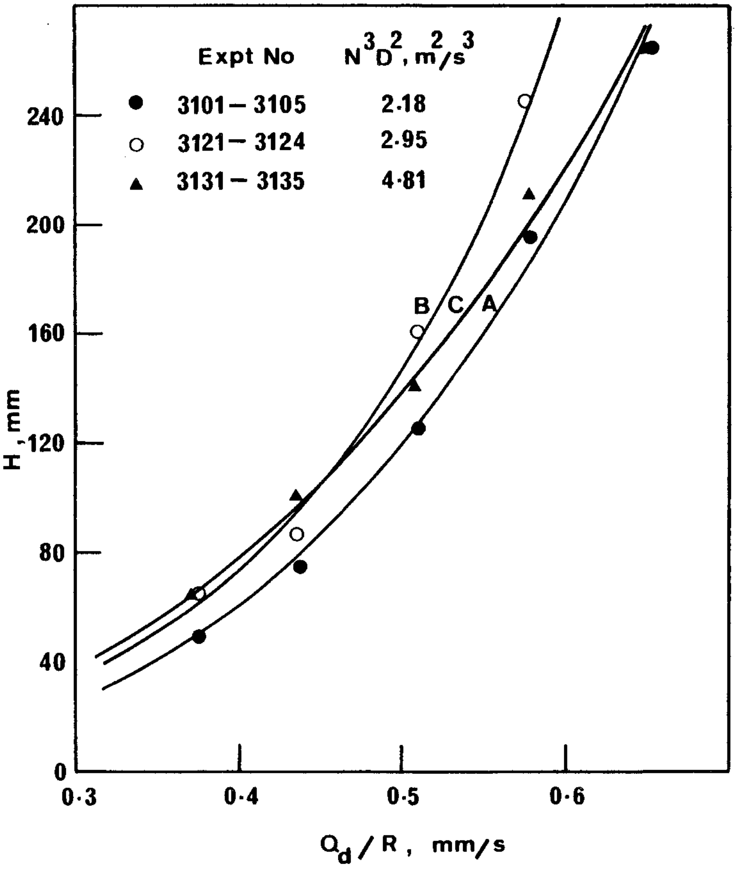


Figure 5.2a Continuous Settling Results: Effect of Mixing Intensity

The data of Fugure 5.2a have been re-drawn on log-log coordinates in Figure 5.2b. The slopes of the lines A, B and C are 3.08, 3.14 and 2.55 respectively. Incidently, these values are not very much different from those of Ryon et al. (1960) and Golob and Modic (1977) whose data gave slopes of 2.5 and 3.1 respectively.

Another mathematical representation of the continuous

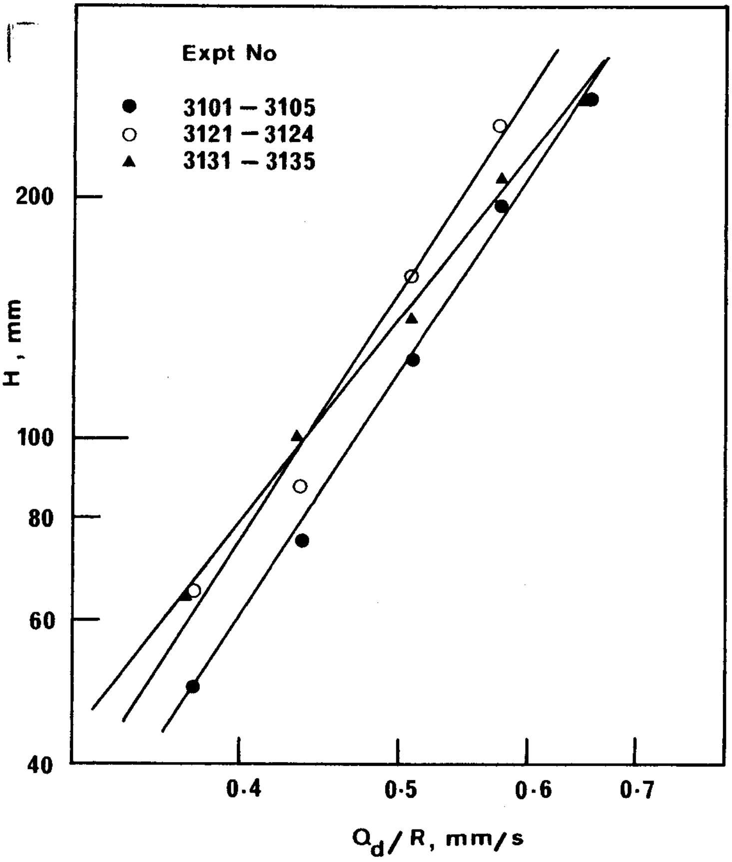


Figure 5.2b Continuous Settling Results

settling results is given in Figure 5.2c which shows a plot of $H/(Q_d/R)$ versus H. Equation (3.17b) proposed by Stönner and Wöhler (1975) has been used to correlate the experimental results. As can be seen from the figure, the results are well-fitted by equation (3.17b).

An additional run was carried out at Q_d/R=14.4 litre/hr and the dispersed to continuous phase ratio of 1 : 1.5 to assess the effect of mixing intensity on the dispersion band height. In this run the mixing speed was varied from 9.78 to 16.63 rps which is much higher than the speed needed for complete mixing

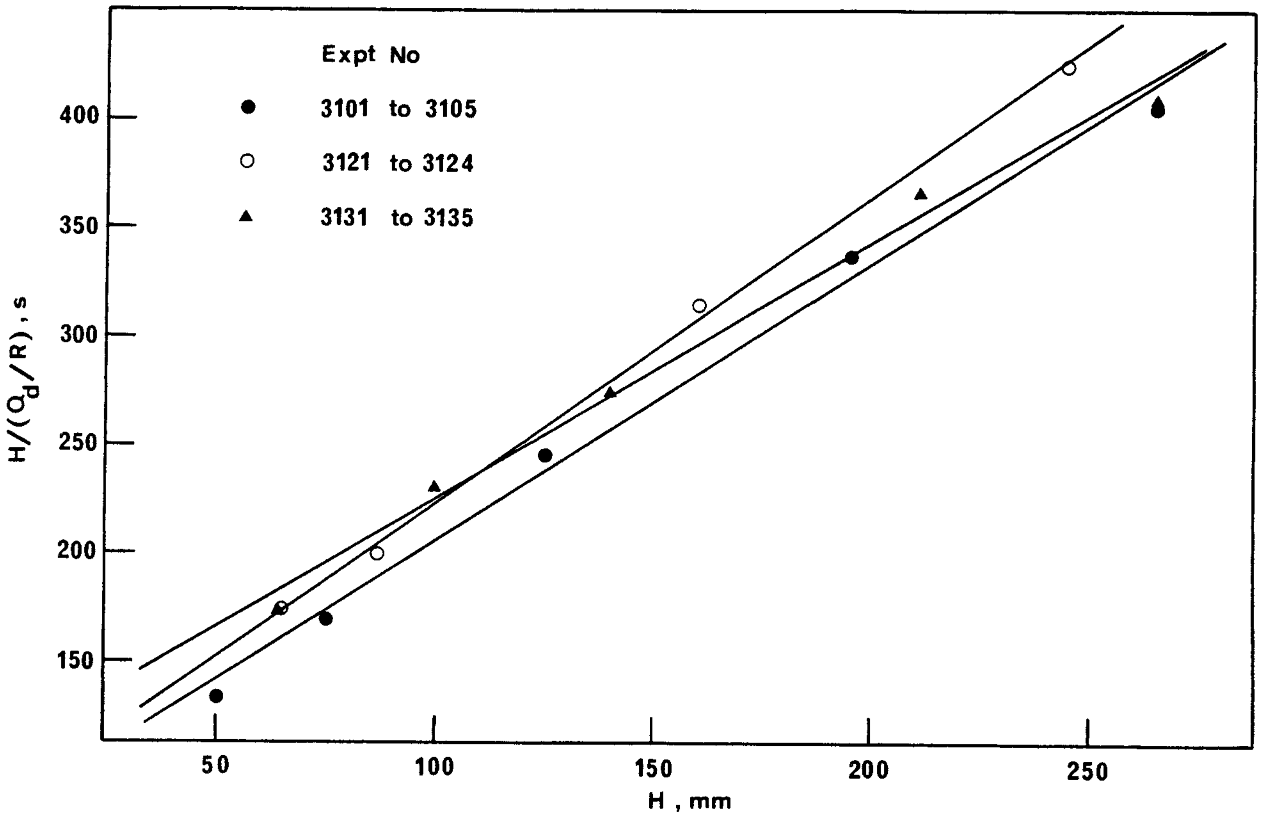


Figure 5.2c Continuous Settling Results

for the liquid/liquid system used, and the average residence time of the dispersed phase in the mixing tank was 26 seconds. At mixing speeds of 16.63 and 14.98 rps, the dispersion entered the settler in the form of periodic small packets due to jerky oscillations of the liquid surface in the mixing tank. This disturbed the dispersion band in the settler due to which it was not possible to attain the steady state at these mixing speeds. It was however possible to attain steady state dispersion in the settler at lower mixing speeds (9.78 to 13.45 rps). In these experiments the dispersion band height did not change with the mixing speed and its average value was found to be equal to 180 mm. The outcome is not surprising in view of the discussion on the effect of mixing regime given in Section 3.2.2. The range of mixing regime investigated falls in a range of operation where the batch or continuous characteristics do not change significantly with increasing mixing intensity. This feature may be explained in the following manner :

The drop size distribution produced by a mechanical mixer is the result of a dynamic equilibrium between the opposing mechanisms of droplet break-up and re-coalescence. Increased mixing intensity affects both mechanisms simultaneously; higher shearing forces enhance droplet break-up, whereas higher collision frequency increases the re-coalescence rate.Thus, the final result may only be a moderate change in the average drop diameter and an even more mild effect on the "tail" end of the size distribution (smallest drops) which is relevant to continuous settling. Moreover, the effect of average drop size of the drops entering the settler tends to become negligible when the average residence time of the drops in the dispersion band is much larger than their life expectation.

ii) Continuous Settling - Effect of Feed Dispersion Concentration (Phase Ratio)

The effect of feed dispersion concentration (phase ratio) on the dispersion band height was investigated under aqueous

Table 5.1 Effect of Phase Ratio on Dispersion Band Height

Organic/aqueous ratio	1:3	1:2	1:1	1.5:1
Dispersion band height	50	130	225	417

continuous conditions. A total throughput of 40 litre/hr was chosen for this purpose and the mixing speed was kept at 7.88 rps. The results from four experiments in which the ratio of organic to aqueous phase was varied from 1:3 to 1.5:1 show a marked dependence of the dispersion band height on phase ratio (Table 5.1). The results are in agreements with earlier observations (Rowden et al., 1974, Barnea and Mizrahi, 1975d). It has been pointed (Rowden et al., 1974) that for a constant total throughput the dispersion band height passes through a maximum when the dispersed to continuous phase ratio is 2:1. However, one would expect that the maximum dispersion band height to be a function of both the liquid/liquid system properties and phase ratio. Thus the result of an increase in dispersed to continuous phase ratio may not be constant, and a maximum dispersion band height may be expected in different systems at different phase ratios.

The results given in Table 5.1 corroborate the general fact that the dispersion band height increases with increase in dispersed to continuous phase ratio. Since it was not possible to explore the effect of higher organic/aqueous ratios because the settler would have flooded, the concept of maximum dispersion band height at a particular phase ratio could not be established for the liquid/liquid system investigated.

On the assumption that continuous phase throughput has no effect, dispersion heights were correlated again by using equation (3.17b) with an average deviation of 14.7% and a maximum deviation of 25.2%.

iii) Batch Settling

With the system used, sedimentation of the dispersed phase droplets took place quickly, whereas the coalescence process was observed to be very slow. Consequently, a dense-packed dispersion was quickly formed and it took as long as 180 seconds before any change in the initial level of the coalescence front could be detected in all the batch settling experiments. Moreover, the movement of the levels of sedimentation and coalescence fronts was followed visually and it was not possible to record both the levels at the same time. Cubic or higher order polynomials were fitted to the sedimenting and coalescence levels data. Fitted polynomials were then used to regenerate the heights of both the fronts as a function of time which, in turn, were used to calculate the total batch decay height, h. Fitted total heihgts of six batch experiments are given in Table 5.2 (batch experiments 3105B1,B2, 3124B1,B2 and 3134B1,B2 correspond to continuous experiments 3101-3105, 3121-3124 and 3131-3135 respectively). This table also gives the initial batch dispersion height, h_o, and the primary break time, t_B, for each experiment. It can be seen that the primary break times for experiments 3124B1,B2 are on the average 16 and 13% higher than those for 3105B1,B2 and 3134B1,B2 respectively.

Table 5.2 Batch Settling Results

Expt No.	3105B1	3105B2	3124B1	3124B2	3134B1	3134B2
h_o (mm)	199.5	199.5	201.0	201.0	201.5	201.5
t_B (s)	575	595	673	688	590	618
t s	h mm	h mm	h mm	h mm	h mm	h mm
180	-	-	83.6	-	83.8	-
190	78.6	77.0	79.6	-	78.4	-
200	74.7	72.0	75.5	79.5	73.2	83.2
210	70.6	67.4	71.3	75.5	68.2	80.6
220	66.4	62.9	67.1	71.8	63.4	77.2
230	62.2	58.7	62.8	68.1	58.8	73.3
240	58.0	54.6	58.7	64.5	54.3	68.9
250	53.8	50.9	54.6	60.8	50.1	64.3
260	49.7	46.7	50.6	57.0	46.0	59.6
270	45.7	43.1	46.8	53.1	42.2	54.9
280	41.9	39.6	43.2	49.0	38.7	50.4
290	38.3	36.3	39.7	44.9	35.5	46.2
300	35.1	33.3	36.6	40.8	32.6	42.3
310	32.2	30.7	33.6	36.8	30.0	38.8
320	29.8	28.6	31.0	33.0	27.7	35.7
330	28.0	26.9	28.7	29.6	25.6	33.0
340	26.7	26.0	26.7	26.7	23.8	30.6
350	26.2	25.8	25.0	24.5	22.0	28.4
360	-	-	-	23.3	20.3	26.4

5.2 Spray Column Apparatus

A schematic diagram of the spray column apparatus is shown in Figure 5.3. A QVF glass column of 100 mm inner diameter and 700 mm length was used. To the column was attached a 100 mm to 150 mm reducer to accommodate the dispersed phase distributor. The distributor consisted of a 10 mm thick teflon plate of 115 mm diameter in which a total of 184 sharp-edged stainless steel syringe needles of 0.69 mm inner diameter were arranged on a triangular pitch of 6 mm. The cylindrical stainless steel assembly holding the distributor plate was filled with stainless steel spring packing to circumvent channelling and allow a more or less uniform delivery through all the nozzles. The heavy dispersed phase was recycled continuously from a reservoir to a constant head tank by a glass centrifugal pump (QVF type GPB 3/30A) and the light continuous phase kept stationary. A sintered glass filter was installed in the line between the pump and the head tank to remove any fine haze in the dispersed liquid. From the constant head tank the dispersed phase was fed under gravity to the distributor through rotameters. The coalesced liquid was taken from the bottom of the column and returned to the reservoir through an overflow valve.

5.2.1 Liquid/Liquid Systems and Experimental Procedure

The systems used for the experimental work were water/40% paraffin oil + 60% toluene, and water/60% paraffin oil + 40% toluene, water being dispersed in the organic liquids. Deionized distilled water and technical grade organic liquids were used. Experiments were carried out at 20 to 21°C and the physical properties of the mutually saturated phases at 20°C are given in Table 5.3. A pyknometer was used to measure the density and two Ubbelhode viscosmeters to measure the viscosity. A drop volume method was used to measure the interfacial tension.

Experiments were performed by thoroughly cleaning the apparatus,

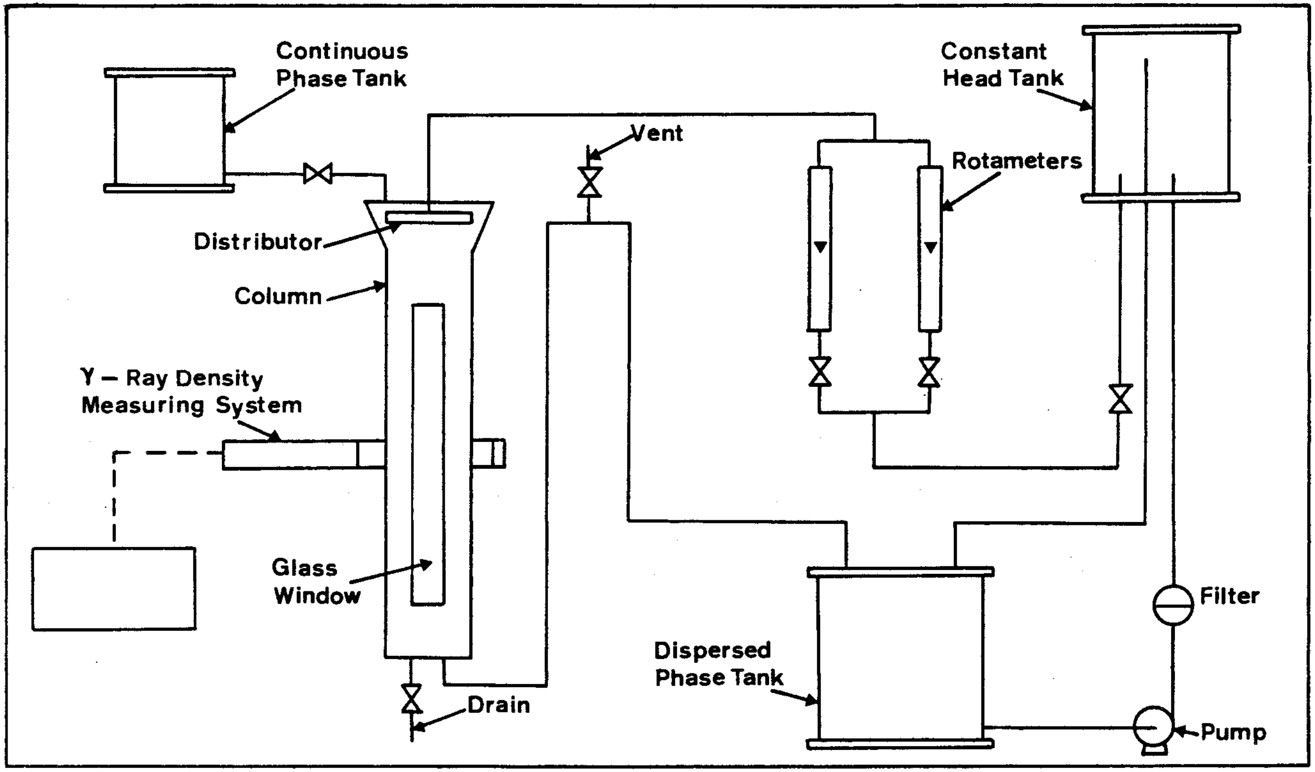


Figure 5.3 Schematic Diagram of Spray Column Apparatus

Table 5.3 Physical Properties of Systems Investigated

Phases Dispersed	Continuous	ρ_d kg/m^3	ρ_c kg/m^3	μ_d mPa s	μ_c mPa s	σ mN/m
Water	40% Paraffin oil + 60% Toluene	997.95	868.39	0.9861	1.7681	38.8
Water	60% Paraffin oil + 40% Toluene	998.23	867.39	0.9983	3.9858	39.3

the method cleaning being the same as that given for the mixer-settler in Section 5.1.1. After cleaning,the dispersed phase storage tank and column were filled with distilled water to remove air from the pipelines and distribution nozzles. The organic liquid (continuous liquid) was then added to fill the column up to the required height.

Before taking the measurements the system was run at a low dispersed phase throughput for about 24 hours to achieve saturation of the phases. The dispersed phase throughput was then fixed at a chosen value and the dispersed phase again cirulated for about 45 minutes to attain the steady state. For each throughput the behaviour of steady state and decaying dispersions were separately recorded (a decay profile was only recorded when the steady state height was more than 50 mm).

For dispersions at steady state the variation in drop diameter with height was determined photographically by using a Nikon F-2 camera and a special plane glass window attached to the column with the intervening space filled with the continuous phase. At each flow setting photographs were taken of the drops entering the dispersion, at the passive interface, in the middle of the dispersion and at the active or coalescing interface. Sideways illumination was used behind a diffuser paper wrapped around the most portion of the column. A high-speed film, Ilford HP 5, 400 ASA, was used at camera settings of 1/80 and 1/125 s at f8. The drop sizes were analysed by using projected images and a frequency histogram of apparent drop diameters obtained. Drops that were out of focus or partially obscured were ignored. This data was then corrected for the degree of photographic enlargement determined in separate experiments in which a uniform steel tube of known diameter was photographed close to the wall of the column. The variation in hold-up with height was determined by the γ-ray absorption technique, the locations of measurements being the same as those mentioned for the drop diameter measurements.

The decay of a steady state dispersion was studied by suddenly closing the gate valve between the constant head tank and rotameters. The levels of the coalescing and sedimenting interfaces were then photographed every two seconds. This was done by using a Nikon intervelometer MT-1 connected to the motor-driven camera.

5.2.2 Results

i) Dispersions at Steady State

The steady state dispersion band height as a function of dispersed phase throughput per unit area is plotted in Figure 5.4a for the two systems investigated. The curves in this figure are similar to the results reported by other workers (Smith and Davies, 1970, Allak and Jeffreys, 1974). The data of Figure 5.4a have been redrawn in Figure 5.4b according to equation (3.17b) and it can be seen that the results are well correlated.

A total of thirty one drop size distribution measurements also resulted. To save space all the raw data is not presented here but typical drop size distributions obtained of the drops entering the dispersion band are shown in Figure 5.5.

Sauter mean diameters of drops entering the dispersion and at different positions of the dispersion band are summarized in Table 5.3. This table also lists the dispersed phase hold-up values corresponding to the drop size measurement locations.

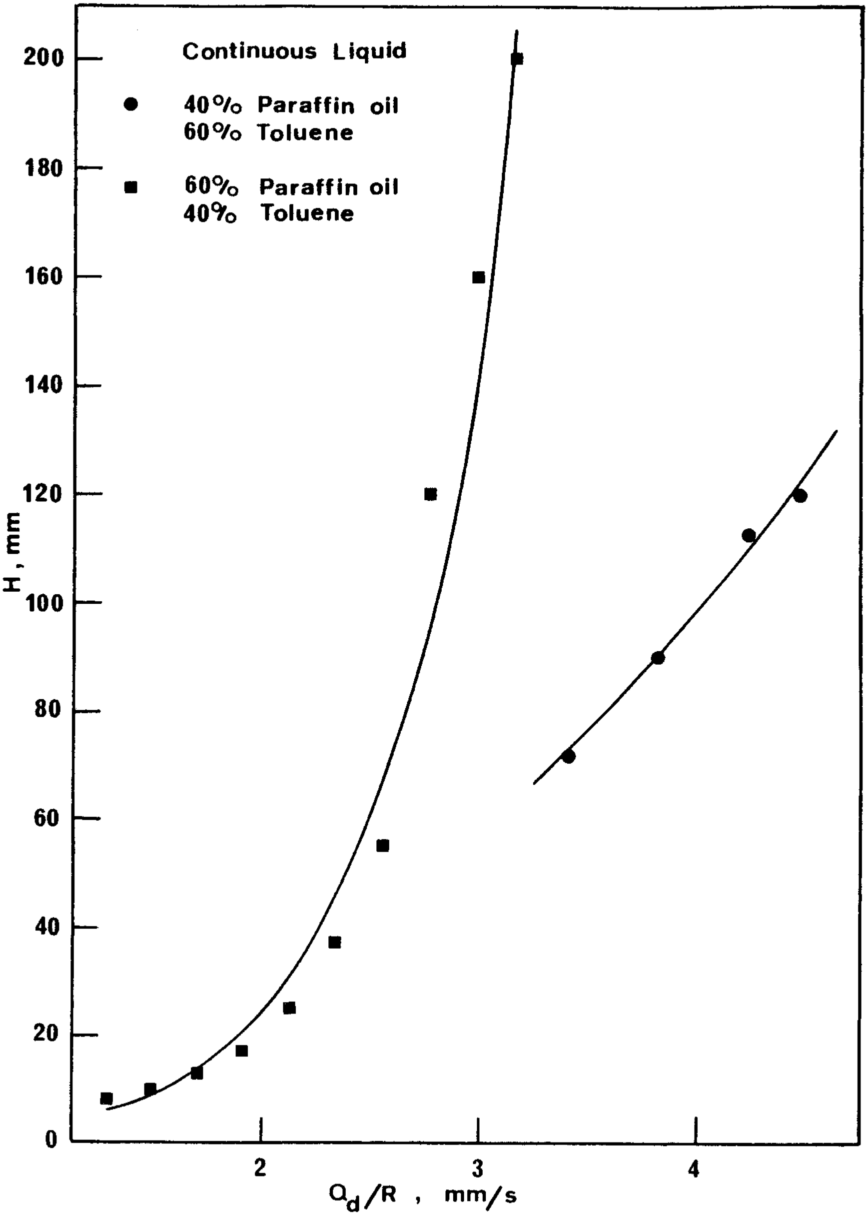


Figure 5.4a Variation of Dispersion Band Height, H, with Dispersed Throughput per Unit Area, Q_d/R

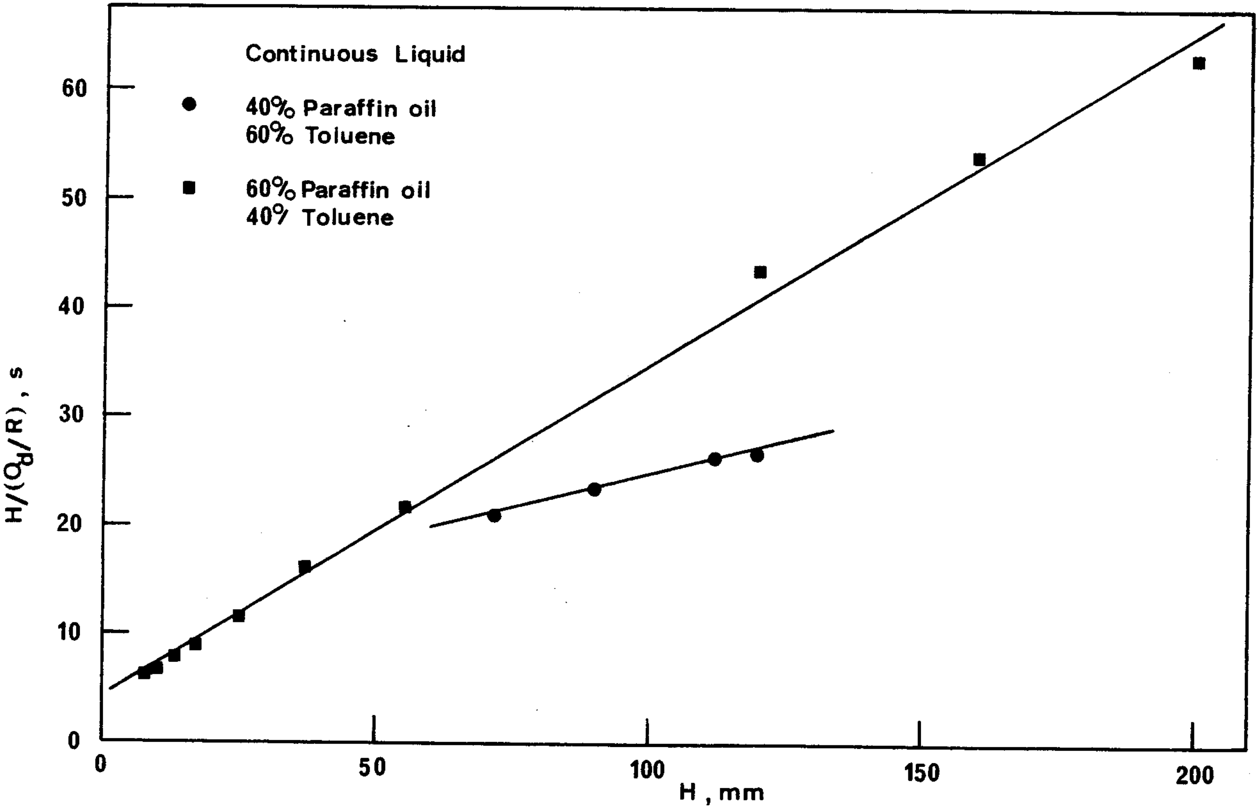
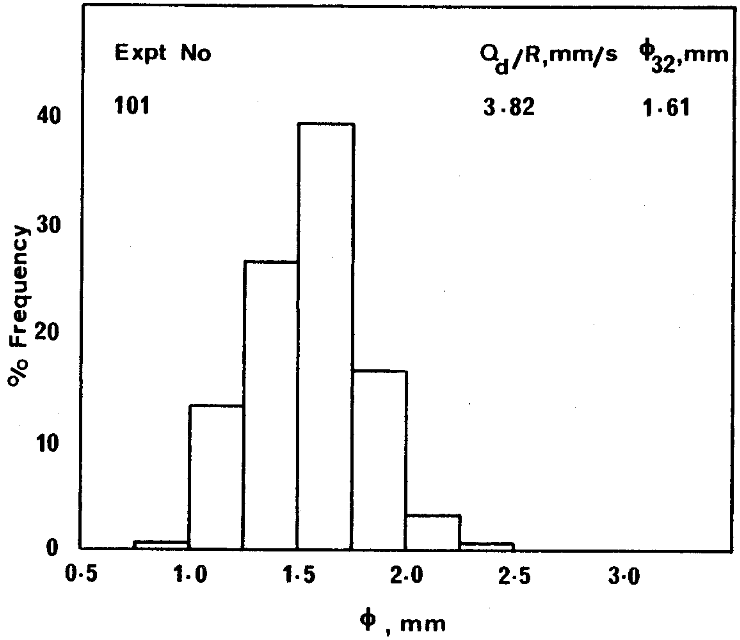


Figure 5.4b Plot of Steady State Dispersion Band Height According to Equation (3.17b)



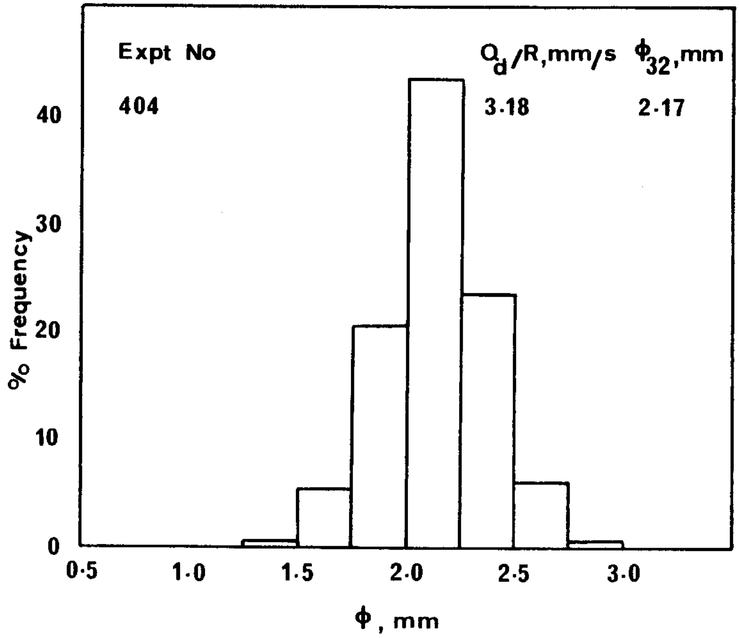


Figure 5.5 Frequency Distribution of Drops Entering the Dispersion Band

Table 5.3 Drop Size and Hold-up at Different Locations of Measurement

Expt No.	Q_d/R mm/s	H mm	Location of Measurement*	ϕ_{32} mm	ε_z
101	3.82	90	E	1.61	-
			S	1.97	0.620
			M	2.49	0.790
			C	3.42	0.870
102	3.40	72	E	1.68	-
			S	1.89	0.600
			M	2.39	0.785
			C	2.86	0.865
103	4.24	112	E	1.69	-
			S	2.07	0.630
			M	3.39	0.790
			C	4.26	0.880
104	4.46	120	E	1.67	-
			S	2.20	0.650
			M	3.54	0.800
			C	4.61	0.888
401	2.97	160	E	2.49	0.081
			S	2.84	0.694
			M	3.45	0.790
			C	3.95	0.887
402	2.55	55	E	3.47	0.081
			M	3.85	0.839
403	2.76	120	E	2.70	0.081
			S	3.29	0.677
			M	3.78	0.806
			C	4.35	0.919
404	3.18	200	E	2.17	0.097
			S	2.36	0.742
			M	2.89	0.774
			C	3.80	0.855
405	2.33	37	E	3.75	-

*E - drops entering the dispersion band, S - sedimenting interface, M - mid-point of dispersion band, C - coalescence front.

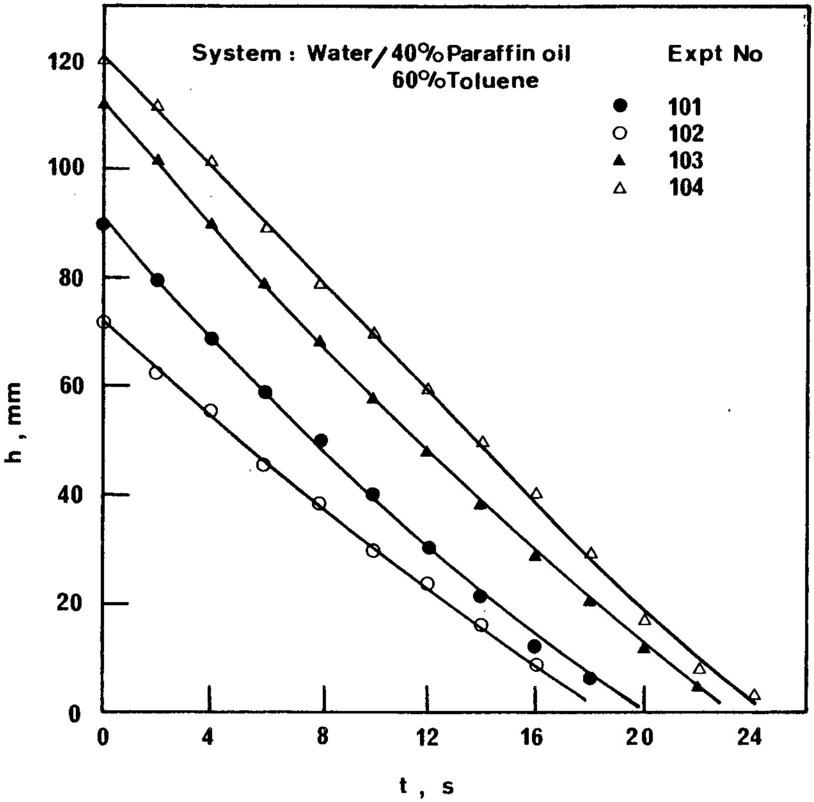


Figure 5.6a Decay of Steady State Dispersions

ii) Decay of Steady State Dispersions

The results for the decay of steady state dispersions are given in Figures 5.6a,b for the systems water/40% paraffin oil+60% toluene and water/60% paraffin oil+40% toluene respectively. The curves in these figures are similar to those reported by Widjaja (1977) and Hartland and Vohra (1978).

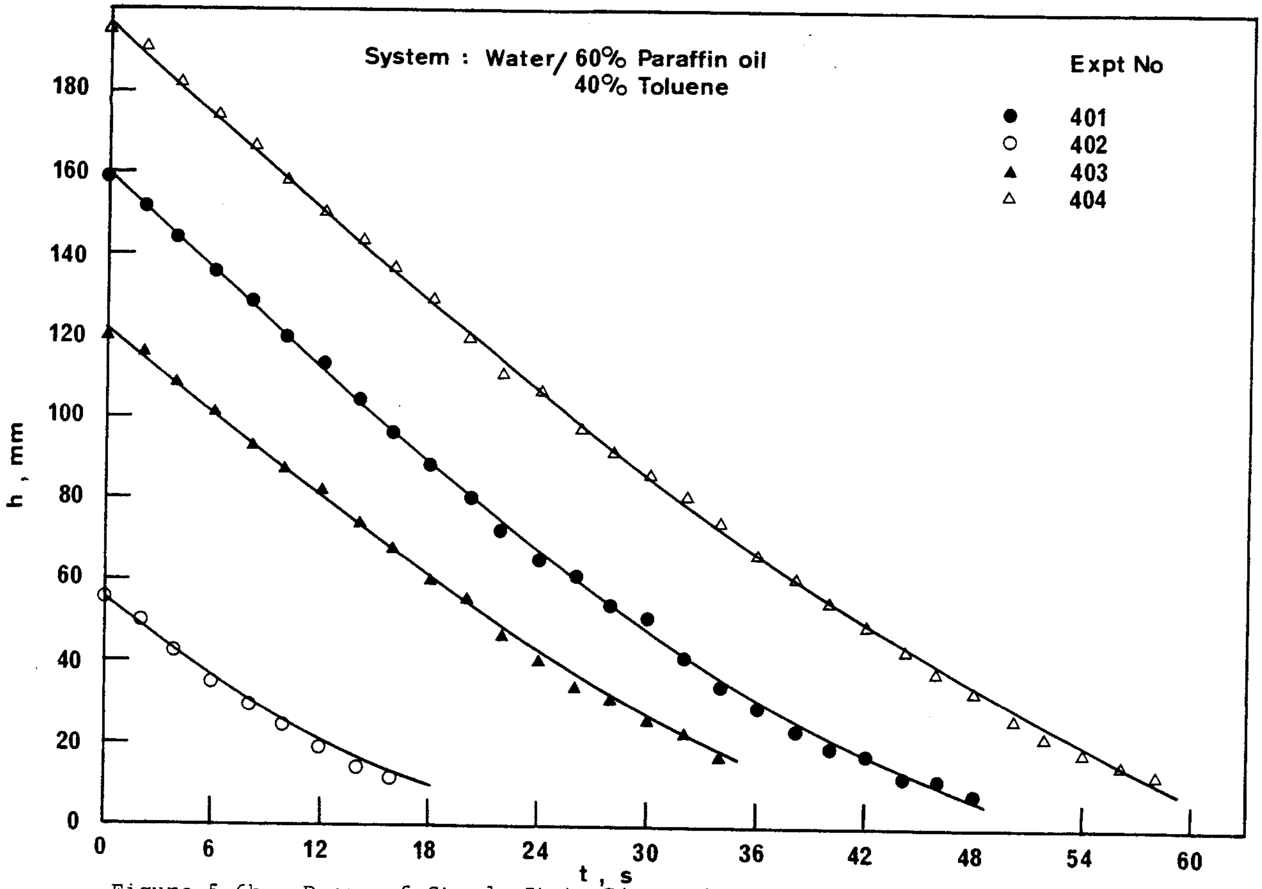


Figure 5.6b Decay of Steady State Dispersions

6. PREDICTION OF STEADY STATE DISPERSION BAND HEIGHT

In this chapter models of coalescence relating batch and continuous settling are discussed and the batch and continuous settling results given in Section 5.1.2 correlated in the light of these models. In Section 6.3 an empirical correlation for the prediction of steady state disparsion band height in a spray column is presented.

6.1 Mathematical Models

6.1.1 Binary Coalescence

Consider a volume of dispersion V in which there are M drops each of diameter ϕ and the dispersed phase hold-up is ε. Although V and ε may change with time, the volume of the dispersed phase, $V\varepsilon = M\pi\phi^3/6$, remains constant. Differentiation with respect to time, t, gives :

$$-\frac{1}{M}\frac{dM}{dt} = \frac{3}{\phi}\frac{d\phi}{dt} \qquad (6.1)$$

If these M drops coalesce in a time τ_b produce M/2 drops, then:

$$-\frac{dM}{dt} = \frac{M - M/2}{\tau_b} = \frac{M}{2\tau_b} \qquad (6.2)$$

Hence the rate of increase in drop diameter is given by :

$$\frac{d\phi}{dt} = \frac{\phi}{6\tau_b} \qquad (6.3)$$

When τ_b is constant and $\phi = \phi_o$ at $t = 0$, integration yields an exponential relationship :

$$\phi = \phi_o\, e^{t/6\tau_b} \qquad (6.4)$$

However, in general, τ_b should be a function of drop size :

$$\tau_b = \tau_{b*}(\phi/\phi_*)^n \qquad (6.5)$$

where τ_{b*} is the binary coalescence time for drops of reference diameter ϕ_*. Setting this equation in equation (6.3) and integrating with the initial condition $\phi = 0$ when $t = -t_o$ gives :

$$\frac{\phi}{\phi_*} = \{\frac{n}{6\,\tau_{b*}}(t + t_o)\}^{1/n} \qquad (6.6a)$$

so

$$\frac{\phi_o}{\phi_*} = (\frac{nt_o}{6\tau_{b*}})^{1/n} \qquad (6.6b)$$

and

$$\frac{\phi}{\phi_o} = (1 + \frac{t}{t_o})^{1/n} \qquad (6.6c)$$

Furthermore, if the reference time is t_* when $\phi = \phi_*$, equation (6.6a) yields :

$$\tau_{b*} = n(t_* + t_o)/6 \qquad (6.7a)$$

and

$$\frac{\phi}{\phi_*} = (\frac{t + t_o}{t_* + t_o})^{1/n} \qquad (6.7b)$$

which become :

$$\tau_{b_*} = nt_*/6 \qquad (6.8a)$$

and

$$\frac{\phi}{\phi_*} = (\frac{t + t_o}{t_*})^{1/n} \qquad (6.8b)$$

when $t_o << t_*$.

Equation (6.8a,b) will be used in Section 6.1.3 to express the drop growth with time in batch and continuous dispersions.

6.1.2 Coalescence at the Disengaging Interface

In a dense-packed dispersion the layer of drops adjacent to the disengaging interface covers a fraction ε_i. In an area R there are thus $4R\ \varepsilon_i\gamma_i/\pi\phi_i^2$ drops of average diameter ϕ_i, if γ_i is a shape factor which allows for their non-sphericity. The number of drops coalescing in unit time is therefore $4R\ \varepsilon_i\gamma_i/\pi\phi_i^2\ \tau_i$, where τ_i is the average time for each drop to coalesce with its homophase. The volume rate of coalescence per unit area of the disengaging interface, ψ_i, is then given by $(4\ \varepsilon_i\gamma_i/\pi\phi_i^2\ \tau_i)(\pi\phi_i^3/6)$, so we may write :

$$\psi_i = \frac{2\ \gamma_i\ \varepsilon_i\ \phi_i}{3\tau_i} \qquad (6.9)$$

At steady state this is equal to the volume throughput of the dispersed phase per unit area, Q_d/R. Thus :

$$\frac{Q_d}{R} = \frac{2\ \gamma_i\ \varepsilon_i\ \phi_i}{3\tau_i} \qquad (6.10)$$

In a decaying dispersion of height h and average hold-up ε the volume rate of coalescence at the disengaging interface is equal to the rate of decrease in dispersion volume, $-d(\varepsilon h)/dt$, so we can write :

$$-\frac{d(\varepsilon h)}{dt} = \frac{2\ \gamma_i\ \varepsilon_i\ \phi_i}{3\tau_i} \qquad (6.11)$$

6.1.3 Formulation of Equations for Batch and Continuous Dispersions

Since in a dense-packed disperion γ_i and ε_i are constant and close to unity, the volume rate of coalescence in equations (6.9 - 11) is effectively determined by the ratio ϕ_i/τ_i. The value of ϕ_i depends on the degree of binary coalescence which has occurred before the drops reach the disengaging interface, and the value of τ_i depends on how it is affected by ϕ_i and the magnitude of gravitational forces pressing on the draining film. The gravitational forces depend on the thickness of the dense-packed layer, which in turn we will assume is a fraction of the dispersion height. Thus τ_i can be expressed in terms of a reference coalescence time, τ_{i*}, which pertains to the drop diameter ϕ_*, and a dispersion height h_* as :

$$\tau_i = \tau_{i*}\left(\frac{\phi_i}{\phi_*}\right)^m / \; f\left(\frac{\varepsilon\, h}{\varepsilon_* h_*}\right) \tag{6.12}$$

Substituting equations (6.8b) and (6.12) into equation (6.9) the volume rate of coalescence per unit area of the disengaging interface is obtained as :

$$\psi_i = \frac{2\,\gamma_i\,\varepsilon_i\,\phi_*}{3\tau_{i*}}\left(\frac{t + t_o}{t_*}\right)^{(1-m)/n} f\left(\frac{\varepsilon\, h}{\varepsilon_* h_*}\right) \tag{6.13a}$$

Since $\psi_* = 2\gamma_i\varepsilon_i\phi_*/3\tau_{i*}$ the above equation can be re-written as :

$$\psi_i = \psi_*\left(\frac{t + t_o}{t_*}\right)^{(1-m)/n} f\left(\frac{\varepsilon\, h}{\varepsilon_* h_*}\right) \tag{6.13b}$$

For the decay of a batch dispersion, $\psi_i = -d(\varepsilon h)/dt$ in equations (6.13a,b). At the reference point where $\varepsilon h = \varepsilon_* h_*$ and $t = t_* >> t_o$, $f(\varepsilon h/\varepsilon_* h_*)$ becomes unity. Thus we can write :

$$-\left\{\frac{d(\varepsilon h)}{dt}\right\}_* = \psi_* \tag{6.14}$$

For a continuous dispersion ψ_i is the dispersed phase throughput per unit area, Q_d/R, h the steady state dispersion height H, and t ($= \varepsilon RH/Q_d >> t_o$) the residence time of the drops in the dispersion.

i) Choice of $f\left(\frac{\varepsilon\, h}{\varepsilon_* h_*}\right)$

There are many forms which $f(\varepsilon h/\varepsilon_* h_*)$ can take. On the one hand the continuous equation should be of the form of equation (3.15) or (3.17c), or some other form which expresses an exponential increase in H with Q_d/R and on the other, the batch equation should predict an S-shaped curve and the associated inflection point when the initial turbulence is high, or an exponential decay alone when the dense-packed dispersion is quickly formed.

A simple form is $f(\varepsilon h/\varepsilon_* h_*) = (\varepsilon h/\varepsilon_* h_*)^p$. Integration of equation (6.13b), using the reference point as the boundary condition, yields the following equation for the batch decay:

$$1 - \left(\frac{\varepsilon h}{\varepsilon_* h_*}\right)^{\alpha} = \frac{\alpha\ \psi_* t_*}{\beta\ \varepsilon_* h_*} \left\{ \left(\frac{t + t_o}{t_*}\right)^{\beta} - 1 \right\} \qquad (6.15)$$

where $\alpha = 1 - p$ and $\beta = 1 + (1 - m)/n$. Equation (6.15) predicts an S-shaped decay curve. The corresponding continuous equation is :

$$\frac{\varepsilon H}{\varepsilon_* h_*} = \left(\frac{\varepsilon_* h_*}{\psi_* t_*}\right)^{1/(\beta-\alpha)} \left(\frac{Q_d}{R}\ \frac{t_*}{\varepsilon_* h_*}\right)^{\beta/(\beta-\alpha)} \qquad (6.16)$$

which is of the form of equation (3.15). In the special case when $m = p = 1$, the equation for batch decay becomes :

$$\log_e \left(\frac{\varepsilon h}{\varepsilon_* h_*}\right) = - \frac{\psi_* t}{\varepsilon_* h_*} \qquad (6.17)$$

which predicts an exponential decay of the batch dispersion. Under the same conditions the continuous equation becomes:

$$\frac{\varepsilon\, H}{\varepsilon_* h_*} = \frac{1}{\psi_*}\ \frac{Q_d}{R} \qquad (6.18)$$

which indicates a linear relationship between H and Q_d/R.

For S-shaped batch curves the form of $f(\varepsilon h/\varepsilon_* h_*)$ should reflect the growth of the dense-packed layer from zero initial thickness to its maximum value in the region of the inflection point and then its return to zero thickness when the dispersion disappears. This condition is not satisfied by the function $(\varepsilon h/\varepsilon_* h_*)^p$. However the condition is approached by the modified function :

$$f(\varepsilon h/\varepsilon_* h_*) = \frac{(1+k)(\varepsilon h/\varepsilon_* h_*)^p}{1+k(\varepsilon h/\varepsilon_* h_*)^q} \qquad (6.19)$$

which passes through a maximum at :

$$\frac{\varepsilon h}{\varepsilon_* h_*} = \left\{\frac{p}{k(q-p)}\right\}^{1/q} \qquad (6.20)$$

Integration of the batch equation then gives :

$$\frac{1}{\alpha}\left\{1 - \left(\frac{\varepsilon h}{\varepsilon_* h_*}\right)^{\alpha}\right\} + \frac{k}{\alpha + q}\left\{1 - \left(\frac{\varepsilon h}{\varepsilon_* h_*}\right)^{\alpha+q}\right\}$$

$$= \frac{(1+k)}{\beta}\,\frac{\psi_* t_*}{\varepsilon_* h_*}\left\{\left(\frac{t + t_o}{t_*}\right)^{\beta} - 1\right\} \qquad (6.21)$$

The continuous equation becomes :

$$\left(\frac{Q_d\ t_*}{R\varepsilon_* h_*}\right)^{\beta} = \frac{\psi_* t_*/\varepsilon_* h_* \cdot (1+k)\,(\varepsilon H/\varepsilon_* h_*)^{\beta-\alpha}}{1+k\ (\varepsilon H/\varepsilon_* h_*)^{q}} \qquad (6.22)$$

If $q = \beta - \alpha (= p + (1-m)/n)$ the above equation becomes :

$$\left(\frac{\varepsilon H}{\varepsilon_* h_*}\right)^{\beta-\alpha} = \frac{(Q_d/R \cdot t_*/\varepsilon_* h_*)^{\beta}}{\psi_* t_*/\varepsilon_* h_* \cdot (1+k) - k(Q_d/R \cdot t_*/\varepsilon_* h_*)^{\beta}} \qquad (6.23)$$

Should $p = q = 1$, equation (6.19) reduces to the hyperbolic function

$$f\left(\frac{\varepsilon h}{\varepsilon_* h_*}\right) = \frac{\varepsilon h/\varepsilon_* h_*}{1/(1+k) + k/(1+k) \cdot (\varepsilon h/\varepsilon_* h_*)} \qquad (6.24)$$

A function of the type given by the above equation will be useful in cases where the sedimentation is relatively fast and the coalescence process rather slow, so that the dense-packed dispersion is quickly formed and the batch decay is exponential.

Moreover, if m in equation (6.13b) is equal to unity the equation for batch settling becomes :

$$\frac{\varepsilon_* h_*}{1+k}\ \log_e\left(\frac{\varepsilon_* h_*}{\varepsilon h}\right) + \frac{k}{1+k}(\varepsilon_* h_* - \varepsilon h) = \psi_*(t - t_*) \qquad (6.25)$$

which predicts a modified exponential decay. In addition the equation for continuous settling is given by :

$$\frac{\varepsilon H}{\varepsilon_* h_*} = \frac{Q_d/R}{\psi_*(1+k) - kQ_d/R} \tag{6.26a}$$

which may be re-written as :

$$\frac{\varepsilon H}{\varepsilon_* h_*} = \frac{1/k \cdot Q_d/R}{\psi_*(1+k)/k - Q_d/R} \tag{6.26b}$$

or

$$\frac{\varepsilon H}{Q_d/R} = \frac{\varepsilon_* h_*}{\psi_*(1+k)} + \frac{k}{\psi_*(1+k)}\,\varepsilon H \tag{6.26c}$$

Equation (6.26c) is of the form of equation (3.17b).

If $f(\varepsilon h/\varepsilon_* h_*)$ in equation (6.13b) is unity, the batch equation integrates to :

$$1 - \frac{\varepsilon h}{\varepsilon_* h_*} = \frac{1}{\beta}\,\frac{\psi_* t_*}{\varepsilon_* h_*}\,\{(\frac{t + t_o}{t_*})^{\beta} - 1\} \tag{6.27}$$

which predicts an exponential type of decay. The continuous equation becomes:

$$\frac{\varepsilon H}{\psi_* t_*} = (\frac{Q_d}{R\psi_*})^{\beta/(\beta-1)} \tag{6.28}$$

which is of the form of equation (3.15).

ii) Choice of Reference Conditions

One is faced with some problems in choosing the reference conditions. Normally it is difficult to locate the phase boundaries in the initial stages due to residual turbulence so that the initial slope cannot be precisely determined. This is also true of the final slope because of the stochastic nature of the coalescence process.

If the variation of h with t in the decay curve exhibits an inflection point, then it is easy to measure the reference quantities h_*, t_* and the slope $s_* = (-dh/dt)_* \simeq \psi_*/\varepsilon_*$ at this point. A decay curve may not possess an inflection point when the initial turbulence is weak. In such a case the initial slope, $s_o = (-dh/dt)_o \simeq \psi_o/\varepsilon_o$ can be easily measured together with h_o. However, one would expect different sets of reference quantities to result in different sets of values of constants correlating the batch data. The effect of reference conditions on the evaluation of unknown constants will be discussed in more detail in the following section.

6.2 Application to Experimental Results

The data of six batch-settling experiments given in Table 5.2 were found to fit very well to an equation of the type :

$$h = C_{6.1} \exp(-C_{6.2}t) \qquad (6.29)$$

the regression coefficient,r, in all cases being more than 0.99.

Equation (6.29) predicts an exponential decrease in h with t and so the batch-settling equations (6.17), (6.25) and (6.27) do also. However, equation (6.17) is not very useful for the present results since its corresponding continuous equation (6.18) indicates a linear increase in H with Q_d/R whereas the continuous results given in Figures 5.2a,b show an exponential increase. Equation (6.27) is based on the assumption that the thickness of the dense-packed layer has no effect on coalescence at the disengaging interface. Moreover, calculations showed that the values of β were not meaningful.

Finally, equation (6.25) was used to correlate the batch-settling results. As expected, the choice of reference conditions had a marked effect on the value of the correlation constant, k. It can be seen from Table 6.1 that the value of k increases with t_*, passes through a maximum and starts

Table 6.1 Correlation Constant k of Equation (6.25) as a Function of Reference Conditions

S. No.	t_* s	h_* mm	$\varepsilon_* h_*$ mm	ψ_* mm/s	1/k	$\frac{\psi_*(1+k)}{k}$ mm/s	$\frac{\varepsilon_* h_*}{\psi_*(1+k)}$ s
Exp.No.3105B1 :							
1	220	66.4	54.3	0.414	12.32	5.51	121.3
2	230	62.2	50.7	0.384	5.39	2.45	111.5
3	240	58.0	47.2	0.355	3.42	1.57	102.8
4	250	53.8	43.8	0.329	2.45	1.13	94.6
5	260	49.7	40.5	0.304	2.14	0.96	90.7
6	270	45.7	37.4	0.282	2.99	1.13	99.4
7	280	41.9	34.4	0.261	6.27	1.90	113.7
8	290	38.3	31.6	0.242	14.60	3.77	122.4
Exp.No. 3105B2 :							
1	220	62.9	51.5	0.371	1428.57	530.94	138.6
2	230	58.7	47.9	0.346	192.31	66.81	137.9
3	240	54.6	44.6	0.322	103.09	33.47	137.4
4	250	50.9	41.5	0.299	65.36	19.85	136.7
5	260	46.7	38.6	0.278	52.63	14.93	136.1
6	270	43.1	35.9	0.259	46.95	12.41	135.8
7	280	39.6	33.4	0.241	58.82	14.41	136.3
8	290	36.3	31.1	0.224	86.21	19.54	137.2

Table 6.1 (continued)

Exp.No. 3124B1

S.No.	t_* s	h_* mm	$\varepsilon_* h_*$ mm	ψ_* mm/s	1/k	$\frac{\psi_*(1+k)}{k}$ mm/s	$\frac{\varepsilon_* h_*}{\psi_*(1+k)}$ s
1	210	71.3	57.6	0.420	16.00	7.13	129.2
2	220	67.1	54.0	0.390	6.50	2.92	120.1
3	230	62.8	50.4	0.362	4.16	1.87	112.1
4	240	58.7	46.9	0.337	2.99	1.34	104.4
5	250	54.6	43.6	0.313	2.38	1.06	98.1
6	260	50.6	40.4	0.291	2.52	1.02	99.5
7	270	46.8	37.4	0.270	3.94	1.34	110.4
8	280	43.2	34.7	0.251	7.43	2.12	121.8
9	290	39.7	32.2	0.233	13.83	3.46	128.7
10	300	36.6	29.8	0.217	24.15	5.46	131.9

Exp.No. 3124B2 :

S.No.	t_* s	h_* mm	$\varepsilon_* h_*$ mm	ψ_* mm/s	1/k	$\frac{\psi_*(1+k)}{k}$ mm/s	$\frac{\varepsilon_* h_*}{\psi_*(1+k)}$ s
1	210	75.5	62.4	0.514	-3.20	-	-
2	220	71.8	59.3	0.476	-4.89	-	-
3	230	68.1	56.3	0.440	-18.05	-	-
4	240	64.5	53.4	0.408	6.84	3.19	114.3
5	250	60.8	50.4	0.377	2.44	1.30	94.8
6	260	57.0	47.4	0.349	1.34	0.82	77.7
7	270	53.1	44.4	0.323	0.75	0.57	59.0
8	280	49.0	41.2	0.299	0.41	0.42	40.1
9	290	44.9	38.0	0.277	2.11	0.86	93.3

Table 6.1 (continued)

Exp.No. 3134B1 :

S.No	t_* s	h_* mm	$\varepsilon_* h_*$ mm	ψ_* mm/s	1/k	$\frac{\psi_*(1+k)}{k}$ mm/s	$\frac{\varepsilon_* h_*}{\psi_*(1+k)}$ s
1	220	63.4	51.2	0.443	13.99	6.64	107.8
2	230	58.8	47.5	0.406	5.43	2.61	98.8
3	240	54.3	44.0	0.372	3.08	1.52	89.3
4	250	50.1	40.6	0.341	2.03	1.03	79.7
5	260	46.0	37.3	0.313	1.69	0.84	75.0
6	270	42.2	34.2	0.286	2.26	0.93	82.8
7	280	38.7	31.2	0.263	4.41	1.42	96.8
8	290	35.5	28.4	0.241	9.40	2.50	106.7
Exp.No. 3134B2 :							
1	220	77.2	64.6	0.523	-13.76	-	-
2	230	73.3	61.5	0.483	7.33	4.02	112.1
3	240	68.9	57.9	0.446	3.05	1.81	97.9
4	250	64.3	54.1	0.411	2.07	1.26	88.7
5	260	59.6	50.2	0.380	1.56	0.97	80.6
6	270	54.9	46.2	0.351	1.16	0.76	70.7
7	280	50.4	42.3	0.324	1.52	0.81	78.7
8	290	46.2	38.6	0.299	4.36	1.60	105.1

decreasing again. The value of $\psi_*(1+k)/k$ decreases with t_*, reaches a minimum (corresponding to the maximum value of k) and then increases again. This shows that the use of diferent reference conditions would predict widely different values for the dispersion band height in a continuous settler. To solve this dilemma, straight lines were fitted to the coalescence front data to find the average slopes(coalescence rate). In four out of six sets in Table 6.1, the value of ψ_* (also coalescence rate) for k to be maximum or $\psi_*(1+k)/k$ to be minimum almost matched with the corresponding average slope, whereas the remaining two values of ψ_* were not far away from the corresponding average slopes. Moreover, it was found that the value of ψ_* corresponding to the average coalescence rate (slope) of the batch curve resulted in k values which predict well the dispersion band height in the continuous settler. Golob and Modic (1977) also arrived at similar conclusions while correlating the batch and continuous settling (see Section 3.2.3).

Table 6.2 compares the experimental and predicted continuous heights calculated by using equation (6.26a) and the maximum value of k (or minimum value of $\psi_*(1+k)/k$) listed in Table 6.1. The continuous experiments 3101-3105, 3121-3124 and 3131-3135 correspond to the batch experiments 3105B1,B2, 3124B1,B2 and 3134B1,B2 respectively. It can be seen that the agreement obtained between experimental and calculated values of H using the maximum value of k of experiment 3105B2 is not good for Q_d/R higher than 0.5mm/s. It is also true that none of the k values listed in Table 6.1 for this particular experiment predict continuous results (3101-3105) satisfactorily. Moreover, the maximum value of k for experiment 3124B2 predicts flooding at $Q_d/R = 0.42$ mm/s, which is much less than the experimental Q_d/R values at which flooding did not take place. Hence,the k value corresponding to $t_* = 260$ s (20 seconds less than t_* for the maximum value of k) was used to predict the continuous results for Experiments 3121-3124. For the remaining four sets the maximum values of k were used to compute

Table 6.2 Continuous Results Compared with Those Calculated from the Batch Results

Exp. No.	Q_d/R mm/s	H(exp) mm	H (pred) mm	
			k=0.47 $\frac{\psi_*(1+k)}{k} = 0.96$ mm/s	k=0.02 $\frac{\psi_*(1+k)}{k} = 12.41$ mm/s
3101	0.374	50	74	70
3102	0.436	75	97	82
3103	0.509	125	131	96
3104	0.578	195	176	110
3105	0.652	265	247	125
			k=0.40 $\frac{\psi_*(1+k)}{k} = 1.02$ mm/s	k=0.75 $\frac{\psi_*(1+k)}{k} = 0.82$ mm/s
3121	0.374	65	78	72
3122	0.436	87	101	97
3123	0.509	160	134	140
3124	0.577	245	175	205
			k=0.59 $\frac{\psi_*(1+k)}{k} = 0.84$ mm/s	k=0.86 $\frac{\psi_*(1+k)}{k} = 0.76$ mm/s
3131	0.371	64	66	68
3132	0.435	100	90	96
3133	0.509	140	129	145
3134	0.578	211	185	227
3135	0.651	265	288	428

the continuous results. The agreement between experimental and predicted heights can be seen to be good in spite of the simplified assumptions used in formulating the batch and continuous equations.

If the hold-up is assumed to be constant equation (6.25) for the batch settling may be simplified to :

$$C_{6.3} \log_e\left(\frac{1}{h}\right) - C_{6.4}h + C_{6.5} = t \qquad (6.30a)$$

A comparison of equations (6.25) and (6.30a) shows that

$$C_{6.3} = \frac{\varepsilon h_*}{\psi_*(1+k)} \qquad (6.30b)$$

$$C_{6.4} = \frac{\varepsilon\ k}{\psi_*(1+k)} \qquad (6.30c)$$

and

$$C_{6.5} = \frac{\varepsilon}{\psi_*(1+k)} \log_e(h_*) + \frac{\varepsilon\ h_* k}{\psi_*(1+k)} + t_* \qquad (6.30d)$$

Under the same conditions the continuous equation becomes :

$$H = \frac{C_{6.3}Q_d/(R\varepsilon)}{1-C_{6.4}Q_d/(R\varepsilon)} \qquad (6.31)$$

The constants ($C_{6.3}$ and $C_{6.4}$) evaluated from the batch settling data given in Table 5.2 are listed in Table 6.3. The constants given by Experiments 3105B2 and 3124B2 are not meaningful and the other sets of constants predict either too low or too high continuous heights, indicating that averaging $C_{6.3}$ and $C_{6.4}$ over all observations is not useful and specific reference quantites have to be used in order to correlate the batch and continuous settling satisfactorily.

Mizrahi and Barnea (1970) and Barnea and Mizrahi (1975d) suggested a correlation of nominal settler capacity with batch separation or primary break time (equation (3.19)). Using the same approach the nominal settler capacity based on dispersed phase throughput per unit area (since the phase ratio in the experiments described above was kept constant, namely 1:1.5) was related to a value of H of 200 mm

Table 6.3 Constants of Equations (6.30a, 6.31)

Exp.No.	3105B1	3105B2	3124B1	3124B2	3134B1	3134B2
$C_{6.3}$	113.29	141.63	87.09	31.10	111.63	77.32
$C_{6.4}$	0.42	-0.17	1.00	2.02	0.28	1.07

and the batch separation time, t_B, (seconds) to the batch dispersion height of 200 mm as :

$$\left(\frac{Q_d}{R}\right)_N = 18.14 t_B^{-0.54} \qquad (6.32)$$

It can be seen from Table 6.4 that this correlation is very good with a maximum absolute error of 1.4%.

Table 6.4 Correlation of Nominal Settler Capacity

Exp.No.	t_B s	$(Q_d/R)_N$ mm/s exp	 pred	Error %
3105B1	575	0.600	0.603	- 0.5
3105B2	595	0.600	0.592	1.3
3124B1	673	0.549	0.554	- 0.9
3124B2	688	0.549	0.547	0.4
3134B1	590	0.586	0.594	1.4
3134B2	618	0.586	0.580	1.0

6.3 Empirical Correlation for the Steady State Dispersion Band Height in Spray Columns

It should be possible to estimate the dispersion band thickness from the correlations of physical properties. Correlations available in the literature (equations (3.24-26)) were used to predict the steady state dispersion band height for the two systems investigated. Computed heights, using these three correlations are listed in Table 6.5 (for experiments 406-410 only heights were recorded and drop diameters not measured; predicted diameters using equation (3.6) were used in equations (3.24-26) for these experiments), and it can be seen that these are consistently lower than the experimental heights. The outcome is understandable since these correlations are based on the experiments performed in the single drop or non-jetting region (large drops) and the dispersion band height, H, was shown to increase linearly with Q_d/R, whereas present results were obtained in both single drop and jetting regions and show an exponential increase. A correlation similar to equations (3.24-26) has been developed for the present results to give different constants as:

$$\frac{H}{\phi_o} = 3.56\text{x}10^7 \left(\frac{Q_d/R.\mu_c}{\sigma}\right)^{1.99} \left(\frac{\phi_o^2 \; \Delta\rho g}{\sigma}\right)^{-1.52} \left(\frac{\mu_d}{\mu_c}\right)^{-0.28} \qquad (6.33)$$

Predicted heights are given in Table 6.5 and the agreement with the experimental heights can be seen to be good. Experiments 406-410 were not included in the analyis since the diameters of the drops entering the dispersion band were not measured. Once again, predicted diameters using equation (3.6) were used and the heights calculated. Because of the additional error introduced due to the use of predicted drop diameter, the agreement between experimental and predicted heights for experiments 406-410 is only fair. Thus, if the drop diameter is not available, the correlations of drop sizes given in Sections 4.1.1 and 4.1.2 may be used in conjuction with equation (6.33) to calculate approximately the steady state dispersion band height in a spray column.

Table 6.5 Prediction of Steady State Dispersion Band Height

Exp.No.	Q_d/R	ϕ_o	H(exp)	H(pred), mm			
	mm/s	mm	mm	Equation (3.24)	Equation (3.25)	Equation (3.26)	Equation (6.33)
101	3.82	1.61	90	20.7	17.7	27.7	94.7
102	3.40	1.68	72	18.1	15.6	22.6	68.9
103	4.24	1.69	112	21.8	18.7	28.5	105.6
104	4.46	1.67	120	22.9	19.6	30.8	119.6
401	2.97	2.49	160	12.8	11.0	9.5	145.6
402	2.55	3.47	55	8.8	7.6	4.5	54.6
403	2.76	2.70	120	11.3	9.7	7.6	106.7
404	3.18	2.17	200	15.1	12.8	13.1	220.9
405	2.33	3.75	37	7.7	6.7	3.6	39.0
406	2.12	-	25	7.7	6.7	3.9	40.4
407	1.91	-	17	6.7	5.8	3.1	28.4
408	1.70	-	13	5.7	5.0	2.3	19.2
409	1.49	-	10	4.8	4.2	1.8	12.6
410	1.27	-	8	3.9	3.5	1.3	7.8

7. CONCLUSIONS

Three types of liquid/liquid contactors, namely spray columns, pulsed sieve-plate columns and mixer-settlers have been considered in this work.

All available experimental data (484 data points for 12 liquid/liquid systems from 8 sources) on drop size in spray columns have been used to develop correlations for single drop and jetting regions. A general correlation, treating the entire range of nozzle velocities up to the critical nozzle velocity is also suggested. These correlations predict the drop diameter with average errors of less than 10%.

The drag coefficient for multiparticle systems defined by Barnea and Mizrahi (1975e) was modified and a simple correlation for the prediction of slip velocity in spray columns is presented. From this the dispersed phase hold-up can be calculated if the phase flow rates are known. The correlation applies for $7 < Re_{\varepsilon,1} < 2450$ and hold-up $0.01 < \varepsilon < 0.75$, and predicts two values of hold-up corresponding to loose and dense-packed operation in a spray column.

Mixer-settler, dispersion and emulsion regimes of operation in pulsed sieve-plate columns have been properly defined and empirical expressions for the hold-up of the dispersed phase in terms of physical properties, operating conditions and column geometry in these regimes of operation determined. The proposed correlations are based on 725 data points on 8 solvent dispersed systems from 5 sources and predict the hold-up with average errors of 13.5, 12.4 and 13.7% for the mixer-settler, dispersion and emulsion regions respectively.

It has been shown that no consistent basis in the literature exists for the design of gravity liquid/liquid settlers. The problems associated with designing continuous settlers on the basis of small batch tests are also discussed. Experiments were therefore performed in a single-stage mixer-settler unit to study the continuous settler characteristics. Two batch tests for every continuous settler characteristic were also carried out at the same time. Experimental batch decay profiles were fitted by using the proposed mathematical models and the parameters evaluated used to predict the steady state height in the continuous settler.

Experiments on the coalescence of droplet dispersions were also performed in a spray column using 2 liquid/liquid systems. The dispersion band heights were empirically correlated in terms of physical properties and throughput of the dispersed phase.

NOTATION

A	pulsation stroke (twice the amplitude)
Ar	Archimedes number = $g\Delta\rho\phi_{32}^{3}\rho_c/\mu_c^2$
Ar_G	Archimedes number at $(4\Delta\rho g\phi^2\ P^{0.15})/(3\sigma)$ = 70
B	correction factor defined by equation (2.41b)
C_D	drag coefficient for a single sphere $= (4\Delta\rho g\phi)/(3\rho_c U^2)$
$C_{D\varepsilon,1}$	modified drag coefficient defined by equation (2.39)
$C_{D\varepsilon,2}$	modified drag coefficient defined by equation (2.42)
$C_{D\varepsilon,3}$	modified drag coefficient defined by equation (4.7)
C_I	inertial drag coefficient for a single sphere
$C_{i.j}$	empirical constants (i = 1,2,.. , j = 1,2,..)
c_o	discharge coefficient for flow through holes in sieve plate
D	impeller diameter
d	nozzle or orifice diameter
d_e	inlet pipe diameter
d_{jc}	critical jet diameter
d_o	diameter of holes in sieve plate
E	$= (Af)^3\rho_c/(\lambda\ell\Delta\rho^{3/4}\sigma^{1/4}\ g^{5/4})$
Eö	nozzle Eötvös number = $\Delta\rho d^2 g/\sigma$
e	rate of energy dissipation per unit mass
exp	experimental value
F	force parameter
F_D	resistance force to motion
F_d	force pressing on the film
Fr	nozzle Froude number = $v^2/(gd)$
f	pulse frequency

g	acceleration due to gravity
H	steady state dispersion band height
H(exp)	experimental steady state dispersion band height
H(pred)	predicted steady state dispersion band height
h	dispersion height at any time t
h_{co}	height of the coalescing interface in a batch dispersion at $t = 0$
h_{exp}	experimental batch dispersion height at any time t
h_{pred}	predicted batch dispersion height at any time t
h_o	batch dispersion height at $t = 0$
h_*	batch dispersion height at $t = t_*$
J	number of data points
k	model parameter
k_b	reaction rate constant for inactive drops to produce active drops
k_i	reaction rate constant for active drops to coalesce with the active interface
L	bed height or column length
L_e	length of entrance region
L_f	length of fall to the interface
ℓ	plate spacing
M	number of drops or number of drops not coalescing in time t
M_o	total number of drops assessed
m	model parameter
$m_{i.j}$	indices ($i = 1,2,..$, $j = 1,2,..$)
N	impeller speed
N_{min}	minimum impeller speed for complete dispersion
N_u	minimum impeller speed for uniform dispersion

n	model parameter
n_i	number of immobile interfaces
P	physical property group of Hu and Kintner $= (\rho_c^2\sigma^3)/(g\mu_c^4\Delta\rho)$
p	model parameter
p'	viscosity ratio $= \mu_d/\mu_c$
pred	predicted value
Q	total throughput $= (Q_c+Q_d)$
Q_c	continuous phase throughput
Q_d	dispersed phase throughput
Q_n(exp)	experimentally measured value
Q_n(pred)	predicted value
$(Q/R)_N$	nominal total throughput per unit settler area
$(Q_d/R)_N$	nominal dispersed phase throughput per unit settler area
q	model parameter
q'	tortuosity factor
R	settler's or column's cross-sectional area
Re	Reynolds number for a single sphere $= \rho_c U\phi/\mu_c$
$Re_{\varepsilon,0}$	modified Reynolds number $= \rho_c V_s \phi_{32}/\mu_c$
$Re_{\varepsilon,1}$	modified Reynolds number $= \rho_c V_s \phi_{32}/\mu_\varepsilon$
r	regression coefficient
r_c	average rate of coalescence
S	surface area per unit volume
s_o	slope of the batch decay curve at $t = 0$
s_*	slope of the batch decay curve at reference conditions $= (-dh/dt)_*$

T	column or tank diameter
Te	temperature
t	time
t_B	standardized batch separation or primary break time
t_{BS}	batch separation time defined by equation (3.20)
t_o	time when $\phi = 0$
t_*	reference time when $\phi = \phi_*$
U	terminal velocity of a drop in infinite medium
V	dispersion volume
V_c	superficial velocity of the continuous phase
V_D	drop volume
V_d	superficial velocity of the dispersed phase
V_e	inlet velocity
V_s	slip velocity
V_o	characteristic velocity
v	nozzle velocity
v_c	critical nozzle velocity
v_j	minimum jetting velocity
We	nozzle Weber number $= \Delta\rho d v^2/\sigma$
We_T	tank Weber number $= \rho_c N^2 D^3/\sigma$
w	cross-section factor
x_d	radius of circle of contact
z	distance from sedimenting interface

GREEK LETTERS

α	model parameter
β	model parameter

γ	average percentage deviation defined by equation (4.3)
γ_i	shape factor
Δp	pressure drop
$\Delta\rho$	density difference between phases
δ	film thickness
δ_{min}	film thickness at the barrier ring
δ_{max}	film thickness at the apex of the dimple
ε	average hold-up of the dispersed phase
ε_f	feed dispersion concentration $= Q_d/(Q_c+Q_d)$
ε_z	dispersed phase hold-up at a distance z from sedimenting interface
ε_{zo}	dispersed phase hold-up at entrance to dispersion
ε_o	average hold-up of the dispersed phase in a batch dispersion at $t = 0$
ε_*	average hold-up of the dispersed phase at reference conditions
ζ	Boussinesq's "dynamic surface tension"
η	Kolmogoroff length
θ_o	fraction of inactive drops in a batch dispersion at $t = 0$ or fraction of inactive drops in the feed entering the continuous settler ·
κ	plate free area
λ	function of plate free area defined by equation (2.46a)
μ_c	viscosity of the continuous phase
μ_d	viscosity of the dispersed phase
μ_d^*	effective viscosity of the dispersed phase
μ_m	average viscosity $= (\mu_c+\mu_d)/2$
μ_ε	dispersion viscosity

ν_c	kinematic viscosity of the continuous phase
ξ	$= Af(\mu_d^2/\sigma/\Delta\rho)^{1/4}/(\lambda\ell)^{1/3}$
π	$= 3.1416$
ρ_c	density of the continuous phase
ρ_d	density of the dispersed phase
ρ_m	average density $= (\rho_c+\rho_d)/2$
Σ	summation sign
σ	interfacial tension
τ	average single drop/interface coalescence time
τ_b	average drop/drop coalescence time in a dispersion
τ_{b*}	average drop/drop coalescence time for drops of reference diameter ϕ_* in a dispersion
τ_i	average drop/interface coalescence time in a dispersion
τ_{i*}	average drop/interface coalescence time for a drop of reference diameter ϕ_* in a dispersion
τ_{min}	initial drainage time
$\tau_{1/2}$	"half-life" single drop/interface coalescence time
ϕ	drop equivalent sphere diameter
ϕ_c	critical drop diameter
ϕ_{max}	maximum stable drop diameter
ϕ_{min}	minimum stable drop diameter
ϕ_o	average drop diameter at entrance to dispersion
ϕ_T	transition drop diameter defined by equation (2.28c)
ϕ_*	reference drop diameter
ϕ_{32}	Sauter mean drop diameter
ϕ_{32}^0	Sauter mean drop diameter as ε tends to zero
$\bar{\phi}$	average drop diameter

χ	Harkins-Brown correction factor
ψ_i	volume rate of coalescence per unit area of disengaging interface
ψ_o	$= \{-d(\varepsilon h)/dt\}_o$
ψ_*	$= \{-d(\varepsilon h)/dt\}_* = 2\gamma_i \varepsilon_i \phi_*/(3\tau_{i*})$

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