The Mechanics of a Spray Column

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Local and average holdup and drop size distribution as function of flow rates were measured for kerosene drops and water in a countercurrent, 15-cm. I.D., 160-cm. long, spray column. The range of flow rates was 5 to 40 liters/min. of kerosene and 0 to 50 liters/min. of water. At the same pairs of flow rates of the dispersed and the continuous phases in spray columns, three modes of drop packings can be obtained. These are termed, in order of increasing average holdup and increasing regularity of flow patterns, dispersed, restrained, and dense packings. For dispersed packing, at low flow rates of the two phases, the holdup and the drop size are constant along the column. At high flow rates the drop size increases from bottom to top of the column and the holdup increases from top to bottom of the column. The range of flow rates for the operation of a spray column is extended by the use of a conical entry section (Elgin design) at the bottom of the column, by the formation of an equilibrium region in the conical section.

The average holdup increases with increased flow rates of both phases for dispersed and restrained packings, and with decreased flow rates of both phases for dense packing.

The best definitions of flooding in a spray column are either the point of maximum average specific area of the drops, which corresponds to the onset of coalescence in the column, or the start of rejection of drops from the column proper.

The work reported in this paper is part of a continuing study of spray column heat exchangers (9). The voluminous data in the literature on holdup, drop size, and flooding in a spray column are based on observations or assumptions that although some coalescence takes place within the column under normal operating conditions, the holdup and drop size are constant along the length of the column.

Visual observations of the operation of spray columns in this laboratory have shown that the holdup and drop size vary along the column for a wide range of operating conditions. These phenomena were measured quantitatively and from the results a new approach to the understanding of the operation of spray columns, which is an extension of the previous work of Lapidus and Elgin (8), is presented.

The local holdup and the distribution of drop sizes were measured as functions of position in the spray column and flow rates of the two phases. The average holdup was also measured separately. Water was used as the continuous phase and kerosene as the dispersed phase. One column and one set of dispersion nozzles were used. The range of flow rates in terms of superficial velocities—the flow rate of each phase divided by the cross section of the column—was: for the dispersed phase $V_d = 0.475$ to 3.8 cm./sec.; for the continuous phase $V_c = 0$ to 4.75 cm./sec.

EXPERIMENTAL STUDIES

The continuous phase was distilled water and the dispersed phase was kerosene. Both phases were mutually saturated and continuously recirculated. Figure 1 is a scale drawing of the spray column. The column design was based on the design recommended by Blanding and Elgin (3).

The column proper was a glass pipe, 15 cm.-I.D. and 160 cm. long. The distance between the inlets of the kerosene and the water was 195 cm. The settlers and the conical entry section were made of aluminum, with parallel Perspex windows along their lengths at the front and back. The diameter of the settlers was 35 cm. The piping system and the feed tanks were made of aluminum. The valves were made of chrome-plated brass to minimize corrosion in the system.

The kerosene distribution plate was 8.5 cm. in diameter with 130 nozzles arranged in concentric circles 5 mm. apart. The nozzles were stainless steel tubings, 1.5 mm. I.D. and 4 cm. long.

All measurements were carried out at room temperature. The flow rates were measured by calibrated rotameters. The flow rate of each phase was measured at both inlet and outlet of each phase from the column. Control valves at the outlet of each phase were used to maintain constant flow rates and to change or maintain the position of the kerosene-water interface at the top of the column. The accuracy of the flow rate measurements was ± 0.5% at high flow rates and ± 2% at low flow rates. The range of flow rates in this work was 5 to 40 liters/min. of kerosene and 0 to 50 liters/min. of water.

Local holdups in the column proper were measured by a photoelectric system. A light source and a photocell were positioned next to the column, opposite each other. The glass column was covered by dark paper, except for narrow slits, 1 cm. high and 2 cm. wide, for the photocell and light at each location. Measurements were made at four locations ($S = 30, 70, 120, 150$ cm.).

The light source was an ordinary 150-w. light bulb. The photocell was a Weston Photonic model 856. The output of the photocell was amplified and then reduced by a resistor to the 1-mv. range of the recorder used in this work. The accuracy of the voltage reading was ± 0.01 mv. The intensity of the light source at each location was adjusted to the same reading of the recorder, with the column full of water, by controlling the distance of the light source from the column.

The kerosene contained a low, constant concentration of a blue dye, insoluble in water, in order to increase the contrast between kerosene and water.

The photoelectric system was calibrated against holdup by twelve sets of flow rates, for which the local holdup did not vary along the column and was equal to the mean holdup. The range of holdups for the calibration points was 6 to 70%.

The total fraction of light absorbed in the column is due to a combination of light scattering and light absorption in the column. Light scattering is proportional to the specific area of the drops (H/D) and absorption of light is proportional to the volume of the drops. Absorption of light is dominant at high holdups and light scattering at low holdups, with both mechanisms taking place at intermediate holdups. It was determined empirically, however, that up to holdups of 40% the voltage reading of the recorder was proportional to the local average area of the drops and that for higher holdups the voltage reading was proportional directly to the holdup. This method was checked for each run by calculating the average holdup, by integration of the local holdup, calculating the average holdup, and comparing the results with the measured average holdup for the same flow rates. The agreement was excellent, better than ± 1% for holdups under 35% and about ± 2% for holdups above 50%.

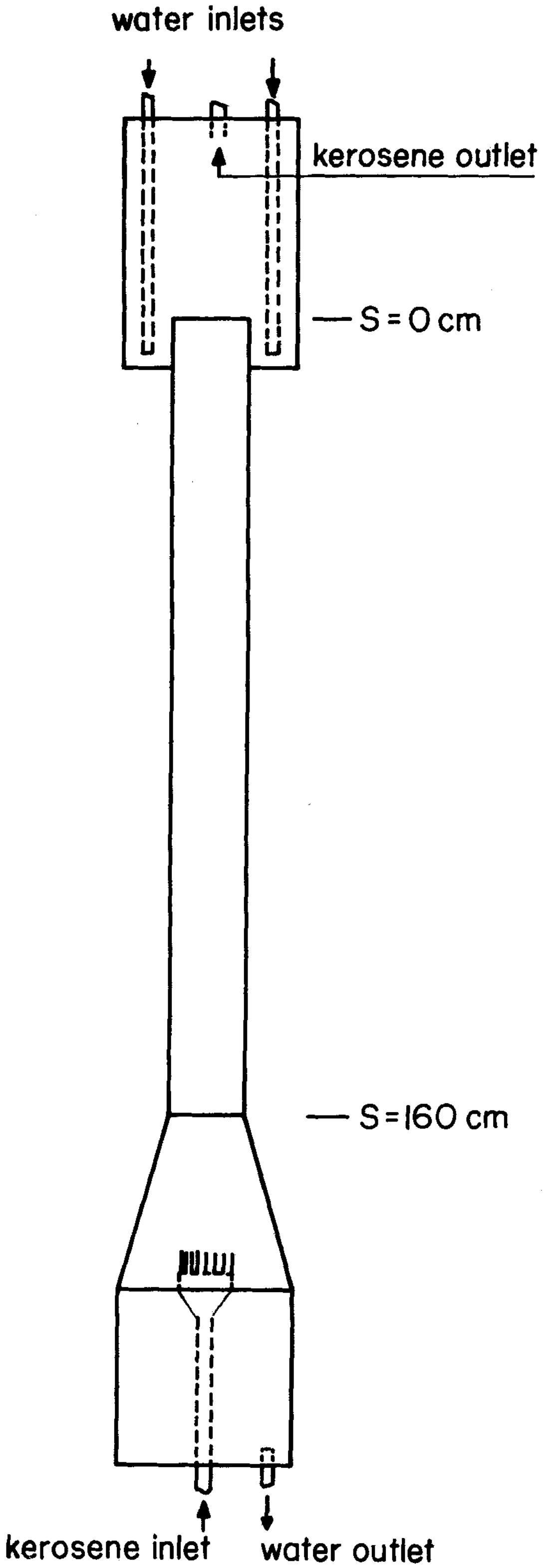

Fig. 1. Scale diagram of the experimental spray column.

The holdup in the upper settler was extrapolated from the holdup distribution curves (Figure 2). The method of estimation of the holdup distribution in the entry cone is illustrated by lines *g* and *h* in Figure 3. A straight line was drawn between the point for the holdup at the bottom of the column proper and a point representing the equilibrium conditions for the lower layer of drops in the conical section.

The mean holdup of the kerosene drops was measured by noting the position of the interface and the lower position of the packing of the drops in the entry cone, when applicable, stopping the flows, waiting for the kerosene drops to coalesce, and measuring the height of the kerosene layer in the column. The kerosene drops leaving the column proper did not, in general, expand into the top settler but continued to flow in the same cylindrical pattern, as in the column, up to the layer or layers of drops below the interface. In the conical section, at high flow rates, a dense region of drops was formed some distance above the nozzles. This distance decreased with increased flow rates. The actual volume of drops in each run and not the volume of the column was used to calculate the mean holdup in the column. The accuracy of mean holdup measurements is estimated as ± 1% for high holdups and ± 30% for low holdups below 10%.

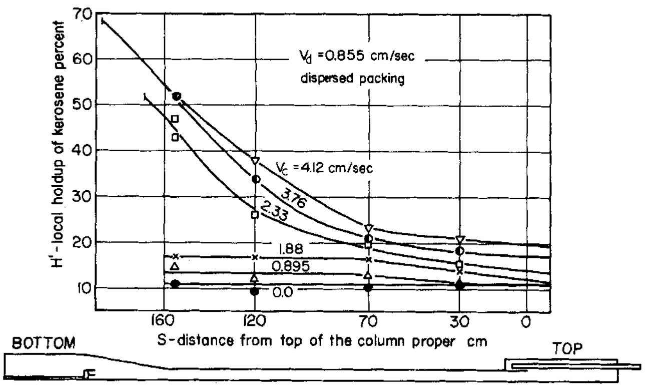

Fig. 2. Local holdup as function of the superficial velocity of water and location in the column for dispersed packing, at one kerosene flow rate.

Drop size distributions were plotted from close-up photographs of the drops, next to scales within the column, at three locations in the column proper (S = 20, 70, and 150 cm.

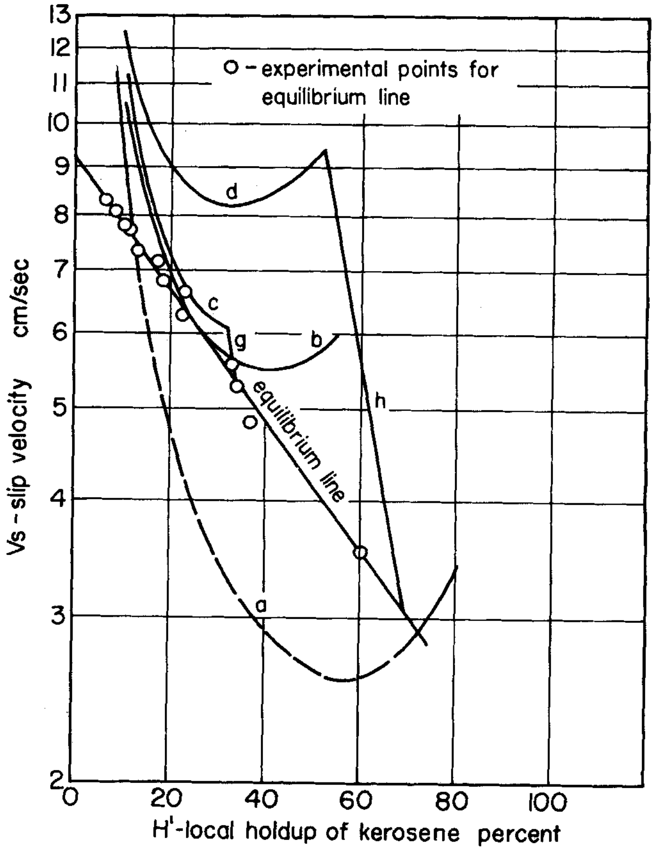

Fig. 3. Experimental equilibrium line and typical operating curves.

from the top of the column proper). Distortion by the curved glass was minimized by enclosing the glass section in a square Perspex box filled with water.

In most runs 150 to 220 drops were measured at each location, and their diameters were calculated as Sauter mean diameters. Except under flooding conditions, plots of drop sizes against the corresponding volume fraction, equal or smaller than that size, on probability paper, gave parallel straight lines. This was also reported by Weaver et al. (*14*). This indicates a normal distribution of drop sizes with the same variance. The average drop size is the median drop size for this type of distribution.

When no or only little coalescence took place in the column, the drops were spherical. With increased coalescence, and particularly toward the top of the column, the shapes of the drops were increasingly distorted to an ellipsoidal form, with the smaller axis parallel to the flow. The volume of the drops in this case was calculated by assuming horizontal symmetry.

MODES OF PACKING

For the same pair of flow rates of the two phases, three modes of packings can be obtained in a spray column. In order of decreasing holdup these modes will be termed: *dense, restrained,* and *dispersed* packings.

Dispersed Packings

In columns of the Elgin design (*3*), with a larger diameter settler at the top, within which the interface is maintained, the mode of packing that is most easily obtained is dispersed packing. It is characterized by relatively low holdups and swirling motion of the drops in the column.

In order to maintain a dispersed packing in the column, it is necessary that the rate of coalescence at the upper interface be higher or at least equal to the flow of the drops. Since the interface area is large and the drop velocities at the top for dispersed packing are high, the rate of coalescence in the upper settler is adequate, even under flooding conditions, to fulfill this requirement.

Dense Packings

In the operation of a spray column at high flow rates, a very dense packing is obtained below the upper interface, which Kintner (*6*) aptly described as a liquid-liquid foam. It is possible to extend the dense packing throughout the column, particularly when holding the interface at the top of the column proper, by starting the operation of the spray column with high kerosene superficial velocities and low water superficial velocities, and maintaining the interface at the top of the column proper. A dense packing builds up from the top of the column, down the column. After a dense packing has been established at the top half or more of the column, it is possible to change the flow rates of the two phases to the desired values, without break up of the dense packing. At steady state, with the dense packing extending throughout the whole column, the interface usually rises 1 or 2 cm. into the upper settler.

For dense packing it is necessary that the rate of coalescence at the interface be equal to the flow rate of the drops. Since the interface was held at the top of the column proper, the lower area of the interface and the slower velocity of the drops, as the dense region is formed, decrease the rate of coalescence below the rate of flow of the drops and a queue of drop layers is slowly built up in the column. If the rate of coalescence at the top is increased, by mechanical or chemical coalescence promoters, the dense packing starts to break up, starting from the top, to the bottom of the column.

The process of building a dense packing in the column can continue into the conical section, if not arrested. This is probably what caused Blanding and Elgin (*3*) to identify a dense packing with flooding of the column.

At low flow rates of the two phases it is possible to control the length of the dense packing by controlling the water holdup. In this type of operation, which had been reported before (*1, 15*), a dense packing is obtained at the upper part of the column and a dispersed packing is obtained in the lower part of the column. A dense packing is characterized by high holdup and orderly, slow motion of drops in the column.

Restrained Packings

A restrained packing is obtained by operating the column with a dispersed packing and then lowering the interface to the top of the column proper. Lowering the interface causes the formation of a denser packing at the top of the column proper and the holdup throughout the column increases. The holdup distribution and the motion of drops for restrained packing are intermediate between those of dispersed and dense packings.

HOLDUP DISTRIBUTION

Typical distribution curves for one kerosene superficial velocity ($V_d = 0.855$ cm./sec.) and six water superficial velocities ($V_c = 0$ to 4.12 cm./sec.), for dispersed packing, are shown in Figure 2. At low flow rates of water the holdup was constant along the column. As the flow rate of water increased, the holdup at the bottom of the column increased more than the holdup at the top of the column. However, a region of constant holdup existed at the bottom of the column. At higher water flow rate no constant holdup region remained and the variation of holdup between bottom and top was considerable. It should be noted that under these conditions the packing of drops extended into the conical entry section. At higher kerosene flow rates, the flow rate of water, above which no constant region of holdup existed, was lower.

In the region of constant holdup, the forces acting on the drop—drag, gravity, and surface—are at dynamic equilibrium and the drops move at constant velocities. In the region of changing holdup the forces acting on the drops are not at equilibrium and both the drops and the continuous phase are accelerating in their respective directions of flow.

Lapidus and Elgin (*8*) proposed that for the vertical flow of solid particles in a fluid, for each particle size, there exists a single function correlating the holdup (H) —the volume concentration of the dispersed phase—with the slip velocity (V_s)—the relative velocity of the two phases:

$$V_s = \phi(H) \tag{1}$$

Weaver et al. (*14*), for flowing organic drops and stationary water, and Beyaert et al. (*2*), for flowing organic drops and countercurrent flow of water, found good correlations, up to the flooding point, between holdup and slip velocity for the operation of a spray column. The slip velocity was calculated by

$$V_s = (V_d/H) + (V_c/1 - H) \tag{2}$$

The holdup was the average holdup measured in the column proper.

Thornton (*13*) correlated the holdup and the superficial velocities of the two phases in a spray column by the function

$$(V_d/H) + (V_c/1 - H) = \overline{V}_0\,(1 - H) \tag{3}$$

where $\overline{V}_0$ is a characteristic velocity, obtained by extrapolating the mean relative velocity of the drops to zero flow rates.

Richardson and Zaki (*11*), in a study of solid-liquid fluidization and sedimentation, proposed a correlation between the velocity of a suspension and the holdup of the form

$$V_c = V_i\,(1 - H)^n \tag{4}$$

where n is a constant for narrow ranges of Reynolds numbers and V_i is the velocity of the settling suspension at zero holdup.

The equilibrium slip velocity (V^*_s), defined as the slip velocity in the constant holdup region of the column, was calculated by the equation

$$V^*_s = (V_d/H') + (V_c/1 - H') \tag{5}$$

where H' is the local holdup. For this equation the local, constant holdup at the lower part of the column was used.

The experimental data was plotted in the form of an empirical exponential function of the equilibrium slip velocity against the corresponding holdup

$$V^*_s = V^o_s \exp\,(-aH') \tag{6}$$

where V^o_s is the equilibrium slip velocity extrapolated to zero holdup and a is an empirical constant. Both V^o_s and a are functions of the physical properties of the liquids employed and the drop size.

The experimental points and the equilibrium line are shown in Figure 3. The numerical constants in this work for kerosene and water at room temperature and drop size of 3.3 to 3.55 mm. were

$$V^*_s = 9.1 \exp\,(-1.6\,H')\ \text{cm./sec.} \tag{7}$$

The value of the equilibrium slip velocity extrapolated to zero holdup (9.1 cm./sec.) is somewhat lower than the value of 12.5 cm./sec. calculated from the correlation of Klee and Treybal (7) for single drops.

THE OPERATING CURVES (*Figure 3*)

For each pair of water and kerosene flow rates, the slip velocity and the local holdup are related by the definition of the slip velocity:

$$V_s = (V_d/H') + (V_c/1 - H') \tag{8}$$

This is an equation of a parabolic curve and a minimum slip velocity exists at some holdup. This curve is designated as the operating curve and it represents all possible relations of slip velocity and holdup in the column for one pair of kerosene and water flow rates.

Four typical operating curves for the same kerosene flow rate and increasing water flow rate from *a* to *d* are plotted together with the experimental equilibrium line in Figure 3.

Curve *a*

This type of operating curve intersects the equilibrium line at two points. For these flow rates it is possible to get equilibrium conditions, and hence steady state, at some point in the column at two holdups, representing the modes of packing of dense packing at the high holdup and dispersed or restrained packings at the low holdup. For the sets of flow rates that give operating curves of type *a*, it was experimentally possible to establish either of these modes of packing at steady state and constant holdup at the lower part of the column.

For the sets of flow rates where the holdup varied in the upper part of the column for dispersed or restrained packings, the holdup distribution is represented by the upper branch of curve *a* at the lower holdups. For dense packings the holdup distribution is represented by the branch of operating curve *a* above the equilibrium line at the high holdup range.

Curve *b*

For the pairs of flow rates, represented by this type of operating curve, the equilibrium line is tangent to the operating curve. For these pairs of flow rates only one mode of packing can be obtained with steady state operation in the column. There is no difference between dense and dispersed packings under these conditions. This curve represents, for a given kerosene flow rate, the maximum water flow rate for which an equilibrium region can be obtained in the column proper. An increase of water flow rate beyond this value will cause rejection of kerosene drops from the bottom of the column proper.

The existence of an equilibrium region in the column or in the conical entry section is necessary to obtain steady state operation of the spray column. When an equilibrium region did not exist in the column proper, rejection from the column proper took place. Operation of the spray column was still possible, as long as the drops did not leave at the water inlet.

Curves *c* and *d*

The conical entry section extends the range of velocities of the two phases, before rejection of the drops at the outlet of the continuous phase starts. The superficial velocities of the two phases in the conical section are lower than in the column proper, and it is possible to obtain an equilibrium condition within the conical section. Increase of the flow rate of either phase causes the equilibrium region within the cone to move down, until the rejection point, where the equilibrium region is below the kerosene nozzles and kerosene comes out of the water outlet, is reached.

Since coalescence starts at flow rates much below rejection and the average drop size increases, the exact situation is more complex, as the conditions for equilibrium are a function of the drop size.

Equations (6) and (8) can be combined to eliminate the slip velocity at equilibrium.

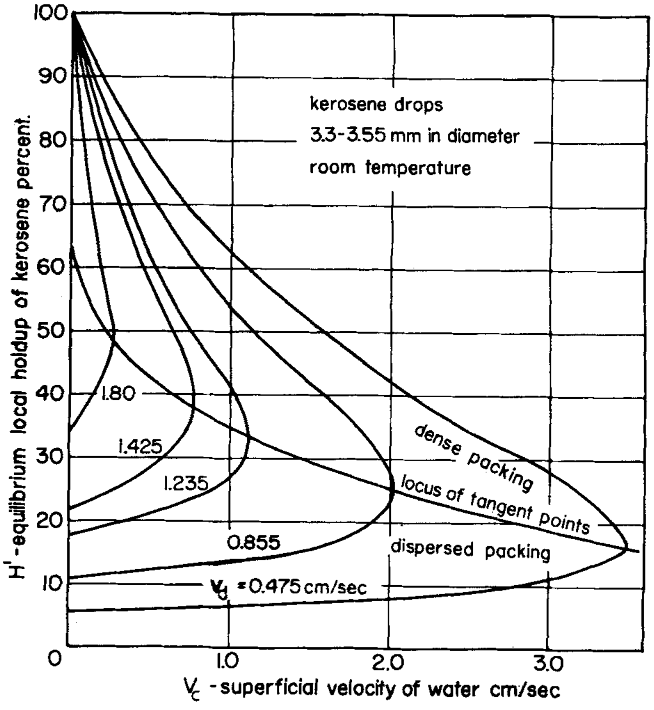

Fig. 4. Equilibrium holdup as function of the superficial velocities of kerosene and water for kerosene drops 3.3 to 3.55 mm. in diameter.

$$V_s^o \exp(-aH') = (V_d/H') + (V_c/1 - H') \quad (9)$$

From Equation (9), the equilibrium holdup as function of the flow rates of the two phases, for kerosene and water at room temperature and drop size of 3.3 to 3.55 mm., were calculated and are shown in Figure 4.

Equation (9) was solved for V_c and the partial derivative of V_c with respect to H was taken and set equal to zero. The locus of the tangential points of the equilibrium line and the operating curve was obtained in the form

$$V_d = V_s^o \left[\frac{1}{1 - H'} + a\right] [H'^2(1 - H')] \exp(-aH) \quad (10)$$

This curve is also plotted in Figure 4.

The difference between operating curves c and d is that in the case of curve c, at a lower water flow rate, the minimum point of the operating curve does not represent an actual condition within the column proper. In the case of curve d, at a higher water flow rate, the minimum point of the operating curve does represent an actual condition within the column proper.

The slip velocity in the column proper, for the situation represented by curve d, decreases with increased holdup down the column to the level of the point of the minimum slip velocity. Below this level the slip velocity and hence the drag forces increase down the column. The combination of higher holdup and higher drag creates favorable conditions for coalescence in the lower part of the column, and this starts the process of coalescence through the rest of the column.

AVERAGE HOLDUP

The average holdup in the spray column is a function of the flow rates of the two phases, the physical properties of the two liquids, the holdup distribution, the drop size, the position of the interface, the length of the column, and if a conical entry section is used with the column. Therefore average holdup data should not be used in scaling up of spray column. For extremely long columns, the average holdup will be close to the equilibrium holdup at the same superficial velocities of the two phases. However, for practical columns the average holdup can be estimated only from measurements of the holdup distribution in a scaled down laboratory column.

The average holdup, for the three modes of packing, for the column and nozzles of this work, as function of the superficial velocities of kerosene and water at room temperature, is shown in Figure 5. The experimental points were omitted for the sake of clarity. The holdup of the dispersed and restrained packings increased with increased flow rates of either phase. Increased flow rates increase the drag forces and the resistance to flow and the drops slow down, and hence the increased holdup. The holdup of dense packing decreased with increase of flow rates of the two phases, since at increased velocities of either phase larger spacings between the drops are required to accommodate the increased flow rates.

DROP SIZE

The average drop size for dispersed packing as function of the superficial velocities of the two phases, at three positions along the column, is plotted in Figure 6. At low flow rates of the two phases the drop size was in the range of 3.3 to 3.55 mm., with a standard deviation of 0.17. The drop size at low flow rates of the two phases was independent of the flow rate of either phase or the positions in the column.

The velocity of the kerosene through the nozzles was in the range of 36 to 188 cm./sec., which is much higher than the range recommended by Hayworth and Treybal (5). The variation of the velocity in the nozzles did not have any significant effect on the drop size within the column.

At some flow rate of the water, for each flow rate of the kerosene, the drop size increased considerably with increase of the water flow rate. The increase in drop size appeared earlier at the top of the column and last at the bottom of the column.

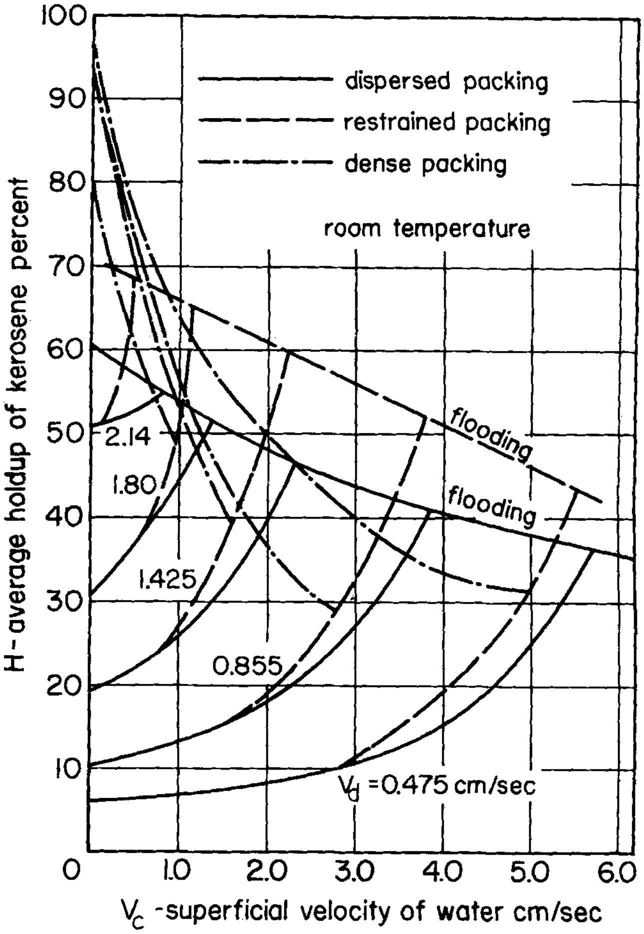

Fig. 5. Experimental average holdup as function of the superficial velocities of water and kerosene for the three modes of packing.

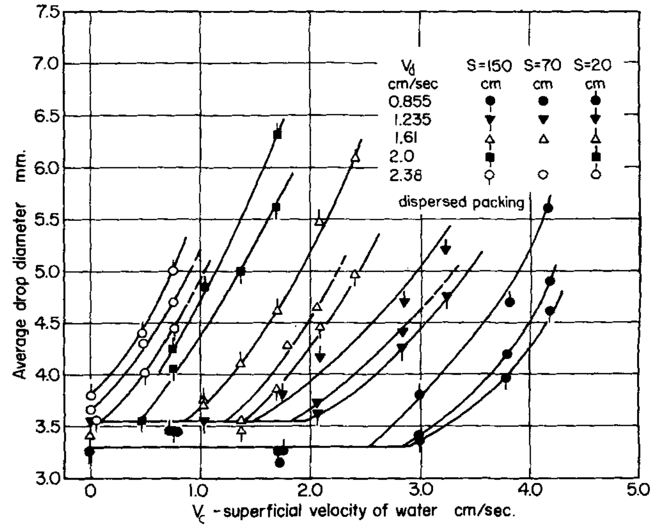

Fig. 6. Average drop size as function of the superficial velocities of the two phases and location in the column for dispersed packing.

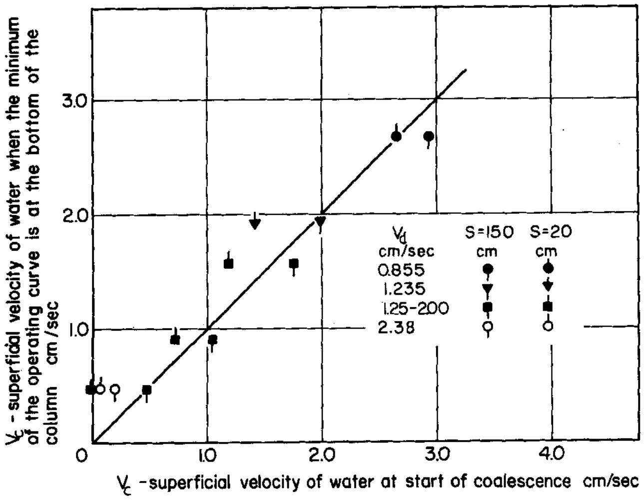

Fig. 7. Correlation of the onset of coalesence with the minimum point of the operating curve at the bottom of the column proper.

It was postulated earlier that coalescence starts when at the bottom of the column the slip velocity increases with increased holdup. This happens when the operating curve is of type *d*, with the minimum slip velocity within the column proper. If this theory is correct, coalescence starts when the operating curve is such that the point of minimum slip velocity is at the bottom of the column proper. This was tested in Figure 7. The abscissa is the superficial velocity of the water at the point where coalescence started, taken from Figure 6 and from additional data at intermediate flow rates for both top and bottom of the column. The ordinate is the water superficial velocity for the same kerosene superficial velocity of the appropriate points for the operating curve where the minimum point of the operating curve was at the bottom of the column proper. A 45-deg. line is also drawn in Figure 7. The good correlation is an indication that coalescence starts at this point.

FLOODING

Lapidus and Elgin (*8*) and Thornton (*13*) defined the flooding point by

$$\left.\frac{dV_c}{dH}\right|_{V_d} = 0 \qquad (11)$$

The average holdup increased with increased flow rate of water for a constant kerosene flow rate up to a maximum value. The flow rates at the maximum average holdup were taken according to the definition in Equation (11) to plot the flooding curves in Figure 5.

The maximum holdup occurred at flow rates much above the start of coalescence and rejection from the column proper, but below the flow rates where rejection from the conical entry section took place.

A few of the many definitions of the visual flooding point are:

1. The start of swirling motion of drops in the lower part of the column (*4*).
2. The rejection of drops from the entry cone (*2, 10*).
3. The set of flow rates where the dispersed phase became the continuous phase (*2*).
4. The formation of a dense packing of drops in the entry cone (*8*).
5. The formation of a dense packing in the column (*3*).

The results of this work show that two definitions of the visual flooding point can be associated with the mechanism of operation of a spray column:

1. The flow rate of the two phases at the maximum value of the specific area of the drops in the column. This definition corresponds also to the point of start of coalescence in the column. This type of flooding curve can be obtained from the points of onset of coalescence from drop size distribution, or from the flow rates of the two phases, for operating curves with a minimum point at the bottom of the column proper.
2. The flow rates for which rejection from the column proper takes place. Flooding occurs at lower flow rates than the previous definition. This type of flooding can be obtained from the locus of the tangential points of the operating curves with the equilibrium line.

CONCLUSIONS

1. It is possible to operate a spray column with up to three modes of packings, at the same flow rates of the two phases.

(a) A dense packing with a high holdup that is obtained when the rate of coalescence is slow and equals the flow rate of the drops.

(b) A dispersed packing with a lower holdup, which is easily obtained in a column of the Elgin design when the rate of coalescence is higher than the flow rate of the drops.

(c) A restrained packing with a holdup intermediate between the other two modes of packing, if the area for coalescence is reduced with a dispersed packing in the column.

2. At low flow rates of the two phases the holdup and drop size are constant along the column. At higher flow rates the holdup increases down the column.
3. Coalescence within the column starts at flow rates which produce an increase of slip velocity with increased holdup. This occurs only in a column with a conical entry section. At high flow rates the drop size increases up the column.
4. For steady state operation of the column, an equilibrium region of constant velocity of drops at the bottom of the column is required. The function of the conical entry section in columns of the Elgin design is to establish this equilibrium region in the conical section and thus enable operation at higher flow rates of the two phases.
5. The average holdup increases with increased flow rates of both phases for dispersed and restrained packings and decreases with increased flow rates of both phases for dense packing.
6. The best definitions of flooding in a spray column are either the point of maximum specific area of the drops, which corresponds to the point of onset of coalescence in the column, or the point of rejection from the column proper.

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NOTATION

a = empirical constant in Equation (6)
D = average diameter of drops, cm.
H = general or average holdup of drops, %
H' = local holdup of drops, %
H/D = specific area of drops, sq.cm./cc.
n = constant in Equation (4)
S = distance along column from top of column proper, cm.
V_c = superficial velocity of continuous phase, cm./sec.
V_d = superficial velocity of dispersed phase, cm./sec.
V_i = velocity of settling suspension at zero holdup, cm./sec.

$\overline{V}_0$ = characteristic velocity in Equation (3), cm./sec.
V_s = slip velocity, cm./sec.
V_s^o = slip velocity at zero holdup, cm./sec.
V_s^* = slip velocity at equilibrium, cm./sec.

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Influence of Resin Selectivity on Film Diffusion-Controlled Ion Exchange

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An analytic solution of the Nernst-Planck equations is derived which applies to a selective resin when film diffusion controls. The selectivity has a marked effect on the rate of exchange for a wide range of diffusivities. The unit-selectivity solution of Schlögl and Helfferich is included as a special case of the more general solution.

Ion exchange in solid-liquid systems is usually regarded as a double replacement reaction which may be written for monovalent cation exchange:

$$A^+Y^- + B^+R^- \rightleftharpoons B^+Y^- + A^+R^- \tag{1}$$

A^+ and B^+ are the exchanging ions called *counterions*, Y^- is the accompanying ion in solution called the *coion*, and R^- is the fixed charged group on the exchanger matrix which ionically bonds with the counterions.

Since the activities of the reacting species are not readily determined (particularly in the exchanger), it is not convenient to describe this reaction in terms of a true equilibrium constant. Frequently another parameter is employed, called the selectivity coefficient α_B^A defined for reaction (1) as

$$\alpha_B^A = (\overline{C}_A\, C_B/\overline{C}_B\, C_A) \tag{2}$$

where C is concentration. The superscript bar indicates the exchanger and the subscripts apply to the counterions.

Since the selectivity coefficient is defined in terms of concentrations, it is not necessarily independent of exchanger or solution composition. Pieroni and Dranoff (*1*) have shown that for the exchange of two monovalent ions, α_B^A is independent of total solution or exchanger concentration but is dependent on the mole fractions of A^+ and B^+ in both phases. It has been shown experimentally, however, that in many systems the equilibrium may be described adequately in terms of a constant selectivity coefficient.

It is generally accepted that the exchange rate is controlled by the diffusion of the reacting species through the solid and/or solution phases. Earlier diffusion models are based on a simple Fick's law approach in which the ex-

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