III. Holdup for Aqueous and Nonaqueous Systems

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Total, static, and operating holdups have been measured for 1-in porcelain and carbon Raschig rings and 1-in. porcelain Berl saddles, employing aqueous solutions of calcium chloride, sorbitol, and a wetting agent as well as pure methanol and benzene. The range of variables covered by this investigation includes liquid rate, 1,000 to 10,000 lb./(hr.) (sq. ft.); viscosity, 0.6 to 185 cp.; surface tension, 23 to 86 dynes/cm.; specific gravity, 0.8 to 1.32.

Equations and charts are presented for estimating holdups for all liquids. The application of holdups for estimating mass transfer coefficients, k_G, and effective interfacial areas, *a*, is discussed.

The total holdups for water, methanol, and benzene can be used to explain why mass transfer coefficients obtained by vaporization of pure liquids in packings seem to depend on gas diffusivity raised to the 0.15 power instead of the 0.67 power, as found in other mass transfer studies. The larger total holdups of nonaqueous liquids result in larger effective interfacial areas in the packing, which mask the effect of the change in gas diffusivity.

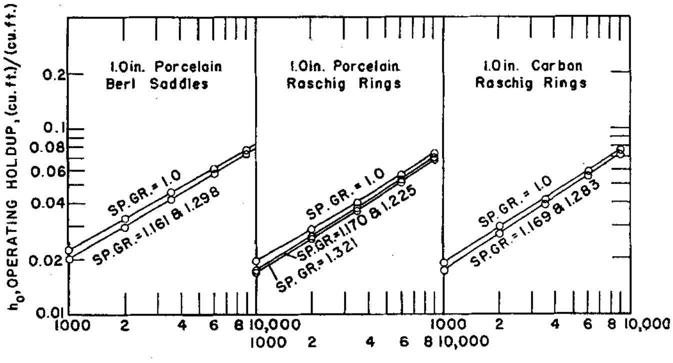

FIG. 2. OPERATING HOLDUP FOR CALCIUM CHLORIDE SOLUTIONS AND WATER AT 20°C. WITH SPECIFIC GRAVITY VARYING FROM 1.0 TO 1.321.

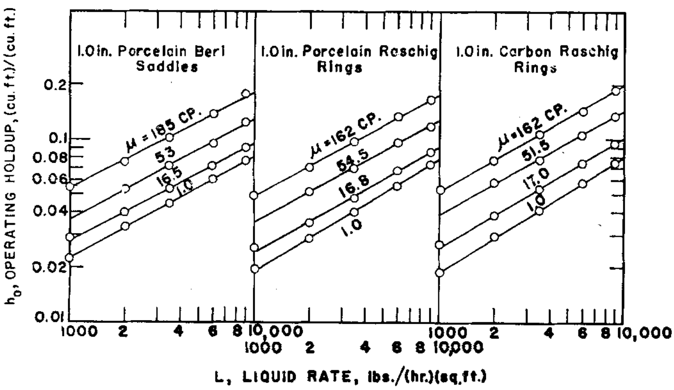

FIG. 1. OPERATING HOLDUP FOR SORBITOL SOLUTIONS AND WATER AT 20°C. WITH VISCOSITY VARYING FROM 1.0 TO 185 cp.

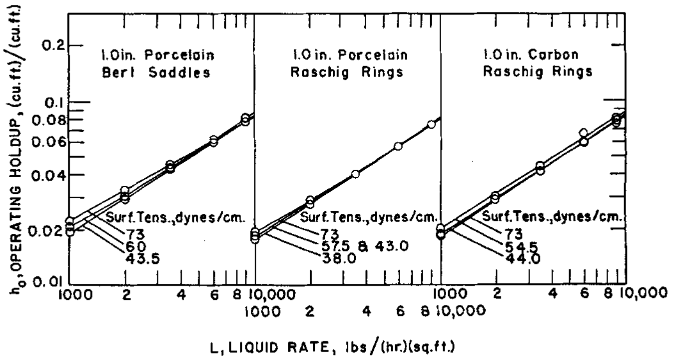

FIG. 3. OPERATING HOLDUP FOR PETROWET SOLUTIONS AND WATER AT 20°C. WITH SURFACE TENSION VARYING FROM 38 TO 73 DYNES/CM.

In the first two parts of this study of the performance of packed columns it was shown that total, static, and operating holdup data could be used in the prediction of mass transfer coefficients for absorption and vaporization in packed columns. Up to the present time mass transfer and holdup studies in packings have been limited almost exclusively to systems employing water as the liquid. For this reason the extension to nonaqueous systems of design methods developed for aqueous systems is of questionable value until appropriate data have been obtained to check the assumptions made.

Attempts have been made to study the vaporization of water and organic liquids in packed columns by Metha and Parekh(*3*) and Surosky and Dodge(*4*). The results of both of these studies indicated that the gas-phase mass transfer coefficient, k_Ga, was proportional to the diffusivity raised to the 0.15 to 0.17 power. This conclusion is in disagreement with all the other mass transfer studies in which a much higher power, in the neighborhood of 0.67, was found to correlate the data. Surosky and Dodge noted that their assumption of a constant effective interfacial area, *a*, for all liquids may have been unjustified, and if the organic liquids wetted the packing surface to a greater extent than water, the effect of diffusivity may have been masked.

The object of this work is to study total, static, and operating holdups in packings to determine the effects of liquid physical properties, such as viscosity, surface tension, and density, and the shape and nature of the packing. By working with water solutions on several packings it is possible to cover a wide range of variables and to develop relationships for the prediction of holdups in aqueous and nonaqueous systems. By working with benzene and methanol on the same packings, data can be obtained to check these relationships for nonaqueous liquids. The holdup data for water, benzene, and methanol can also be used to disprove the validity of the assump-

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Additional tabular material may be obtained from the American Documentation Institute Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., as document 4567, by remitting $1.25 for photoprints or microfilm.

tion that the effective interfacial area, *a*, in packings is the same for all liquids and to help to explain the disagreement between the small effect of diffusivity found by Metha and Parekh (*3*) and Surosky and Dodge (*4*) and the large effect noted by other investigators.

APPARATUS AND PROCEDURE

The apparatus used in this work is the same as that described in Part I of this paper except for a minor modification which consisted of the addition of a gear pump and a small heat exchanger in the line leading to the liquid distributor at the top of the column. These changes made it possible to pump liquids of high viscosity and to hold entering liquid temperatures at 20.0° ± 0.1°C. for all the runs. Water solutions of varying viscosity were prepared by adding sorbitol to the water tank and recycling the solution through the apparatus until a uniform solution of the desired viscosity was obtained. Solutions with viscosities up to 185 cp. could be handled in the apparatus.

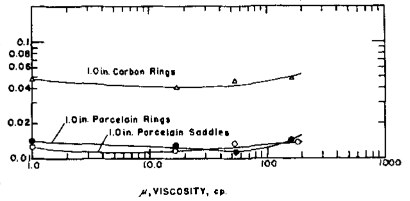

FIG. 4. STATIC HOLDUP FOR SORBITOL SOLUTIONS.

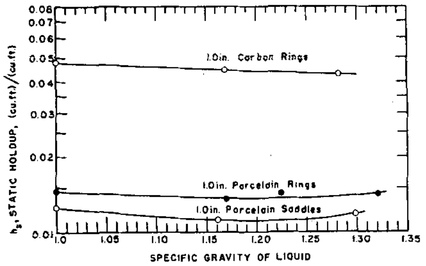

FIG. 5. STATIC HOLDUP FOR CALCIUM CHLORIDE SOLUTIONS.

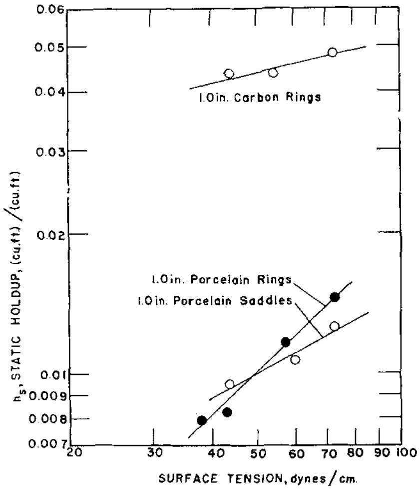

FIG. 6. STATIC HOLDUP FOR PETROWET SOLUTIONS.

Calcium chloride was used to prepare solutions with densities up to 1.32 g./ml. The surface tension of water was decreased to as low as 38 dynes/cm. by the addition of a wetting agent, DuPont Petrowet. To reduce the tendency to foam of these solutions a small quantity of a silicone defoamer, Dow Corning Antifoam A, was added as required. Benzene and methanol served as liquids with densities, viscosities, and surface tensions lower than those attained with any of the water solutions.

Flow rates were measured with rotameters calibrated with each of the liquids employed. Viscosities were measured and controlled with a Rich-Roth Ultra-Viscoson, by use of a gold-plated probe, which was calibrated against glycerol solutions. Surface tension was measured with a Cenco-duNouy interfacial tensiometer, and densities were determined with a Precision specific-gravity balance.

The procedure used was similar to that described in Part I for measuring total, static, and operating holdups except that all runs were made at zero gas rate. One-inch unglazed-porcelain rings and saddles and carbon rings were used. The characteristics of these packings were described in Part I, and in all runs the column was packed so that the dry void fraction was within 1.0% of that reported previously.

EXPERIMENTAL RESULTS

The operating and static holdups for the three packings are shown in Figures 1 to 6 inclusive for the aqueous solutions. The methanol holdups are given in Figure 7, and the benzene holdups in Figure 8. The effects of the physical properties can be determined only qualitatively from some of these figures because it was not possible always to vary one physical property without varying another to some extent. Table I illustrates this point. A series of equations, which can be used to estimate holdups for any liquid on the three packings, was developed by the following procedure. The data for solutions with varying surface tensions were used to determine the effect of surface tension on operating and static holdups. This was possible because these solutions had constant density and viscosity. The data for the calcium chloride solutions were then corrected for the effect of surface tension and used to determine the effect of density. The viscosities of these solutions are low, although higher than the viscosity of water, but the effect of such small changes in viscosities is almost negligible, and slight adjustments could be made after the effect of viscosity had been determined. The effect of viscosity was determined by correcting the sorbitol solution data for the effect of density found previously. The resulting equations are tabulated in Table 2. For the three 1.0-in. packings employed, the operating holdups were found to be independent of the nature of the packing surface, whereas the static holdups were very dependent, as evidenced by the much higher static holdups observed with carbon rings as compared to porcelain rings. The effect of each variable will be discussed separately.

Effect of Surface Tension. The effect of surface tension was found to vary with liquid rate for operating holdup. At low liquid rates, decreasing surface tension resulted in decreasing operating holdup, whereas at high liquid rates de-

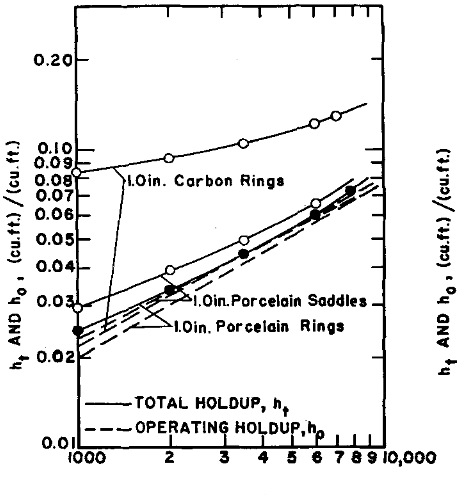

FIG. 7. TOTAL AND OPERATING HOLDUPS FOR METHANOL.

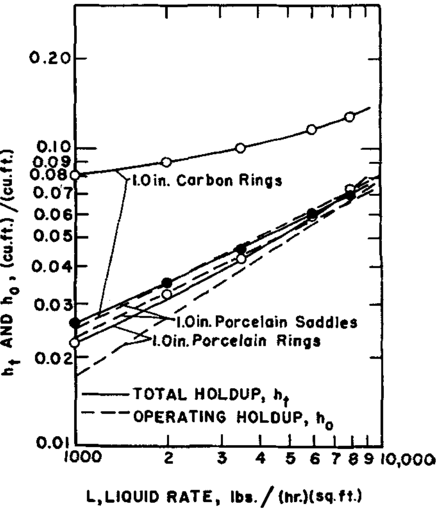

FIG. 8. TOTAL AND OPERATING HOLDUPS FOR BENZENE.

creasing surface tension increased operating holdup. Similar observations were made by Jesser and Elgin (*1*) with 1/2-in. carbon rings, although they found the point of changing effect at much lower liquid rates. The present work and that of Jesser and Elgin (*1*) may result in an erroneous conclusion as to the effect of surface tension because water solutions of wetting agents may have foaming tendencies which are not found in pure liquids of low surface tension. When the present work was started, the Petrowet solutions were found to foam and result in high holdups even at low liquid rates (*1*). The addition of a silicone defoamer, such as Dow Corning Antifoam *A*, eliminated most of the foam at the low liquid rates, but some was still present at higher liquid rates. Unfortunately, there was no way to eliminate the foam completely and so somewhat higher holdups were found than might otherwise have been obtained. Further evidence of this effect of foam formation on the equations which were developed can be obtained by using the equations to estimate the operating holdups of methanol and benzene and comparing them with the experimental values. Although good agreement is obtained in general, the calculated values tend to be high at high liquid rates and low at low liquid rates, as is to be expected if foam formation appeared at the higher liquid rates for the water solutions. The equations appear to be satisfactory, however, for estimating operating holdups of nonaqueous liquids in the range of liquid rates employed in this work, namely, 1,000 to 10,000 lb./(hr.)(sq.ft.).

TABLE 1.—PHYSICAL PROPERTIES OF THE LIQUIDS EMPLOYED FOR HOLDUP MEASUREMENTS AT 20°C.

Liquid	Viscosity, cp.	Density, g./ml.	Surface tension, dynes/cm.
Sorbitol solution	185	1.299	73.0
Sorbitol solution	53	1.268	73.0
Sorbitol solution	16.5	1.215	73.0
Water	1.0	1.000	73.0
Calcium chloride solution	4.5	1.321	86.3
Calcium chloride solution	2.4	1.225	80.3
Calcium chloride solution	1.4	1.170	77.4
DuPont Petrowet solution	1.0	1.000	57.5
DuPont Petrowet solution	1.0	1.000	43.0
DuPont Petrowet solution	1.0	1.000	38.0
Methanol	0.59	0.7998	22.6
Benzene	0.65	0.8780	28.9

TABLE 2.—EQUATIONS FOR ESTIMATING OPERATING AND STATIC HOLDUPS

1. Operating holdup for 1.0-in. Raschig rings for $\mu < 12$ cp.

$$h_o = 0.00039\, L^{0.57}\, \mu^{0.13} \left(\frac{1}{\rho}\right)^{0.84} \left(\frac{\sigma}{73}\right)^{0.925 - 0.262 \log L} \tag{1}$$

for $\mu > 12$ cp.

$$h_o = 0.00025\, L^{0.57}\, \mu^{0.31} \left(\frac{1}{\rho}\right)^{0.84} \left(\frac{\sigma}{73}\right)^{0.925 - 0.262 \log L} \tag{2}$$

2. Operating holdup for 1.0-in. Berl saddles for $\mu < 20$ cp.

$$h_o = 0.00043\, L^{0.57}\, \mu^{0.13} \left(\frac{1}{\rho}\right)^{0.84} \left(\frac{\sigma}{73}\right)^{1.033 - 0.262 \log L} \tag{3}$$

for $\mu > 20$ cp.

$$h_o = 0.00025\, L^{0.57}\, \mu^{0.31} \left(\frac{1}{\rho}\right)^{0.84} \left(\frac{\sigma}{73}\right)^{1.033 - 0.262 \log L} \tag{4}$$

3. Static holdup

$$h_s = c\, \mu^{m} \left(\frac{1}{\rho}\right)^{0.37} \sigma^{n} \tag{5}$$

where c, m, and n have the following values for each packing

Packing	c	m	n
1.0-in. carbon Raschig rings	0.0185	0.02	0.23
1.0-in. porcelain Raschig rings	0.00020	0.02	0.99
1.0-in. Berl saddles	0.00119	0.04	0.55

The effect of surface tension on static holdup is independent of liquid rate, as shown in Table 2; however, the effect is different for each packing, indicating that both the shape and nature of the packing material influence static holdup. The shape of the packing determines the number of points of contact and the horizontal or almost horizontal surfaces on which the static holdup accumulates. The nature of the packing surface will determine the interfacial tension at the liquid-gas-packing contact points and control the degree of wetting and accumulation of the liquid which makes up the static holdup. For this reason, each type of packing material may show a different effect of surface tension on static holdup. For all the packings the static holdup increases as surface tension increases, as might be predicted from an analogy to hanging drops of liquid although there is no direct proportionality for all packings. The absence of a direct proportionality is an indication that there is more than one mechanism for the accumulation and retention of water in packings.

Effect of Viscosity. For viscosities below 12 cp., operating holdups increase with increasing viscosity to the 0.13 power. This is in good agreement with the 0.1 power found by Jesser and Elgin (*1*) in the same viscosity range. For viscosities over 12 cp. for rings and 20 cp. for saddles, the effect changes and the 0.31 power on viscosity represents the data satisfactorily. There is no good reason to account for this change in the effect of viscosity at an intermediate viscosity.

Static holdups are affected very little by increases in viscosity, as shown by the 0.02 to 0.04 power on viscosity. From the definition of static holdup one might expect no effect of viscosity at all, but from an experimental point of view the slow-flowing liquids of very high viscosity can easily cause some of the operating holdup to be mistaken for static holdup.

Effect of Liquid Density. Operating holdups were found to decrease as density increased. The 0.84 power on $(1/\rho)$ is in good agreement with the 0.78 power observed by Jesser and Elgin(*1*) over a more limited range of liquid densities.

The static holdups show a similar, although smaller, effect of density, the power on $(1/\varrho)$ being 0.37.

Effect of Liquid Rate. The operating holdups were found to be proportional to L to the 0.57 power. This is in good agreement with the 0.6 power, which Leva(*2*) found as a good average value for rings and saddles.

Static holdups were found to be independent of liquid rate, as in Part I.

Effect of the Packing Surface. Operating holdups are independent of the nature of the packing surface. It is probably safe to assume that they can be estimated for any packing material by means of the equations developed from the unglazed-porcelain and carbon packings.

Static holdups, however, vary widely for different packing materials. Carbon rings have static holdups which are approximately three times as great for water, thirteen times as great for methanol, and eleven times as great for benzene as for the corresponding porcelain rings. A portion of the larger static holdups in the carbon packing may be accounted for by a porous surface. Thus the static holdup as determined with carbon rings which have been soaked in water for 2 weeks is about 25% greater than that found when dry rings are employed. When carbon rings were soaked in water, benzene, and methanol it was found that they gained several percent in weight up to about a week and the relative gain in weight was approximately proportional to the static holdup found with these liquids. It is unlikely, however, that porosity can account for more than a fraction of the total static holdup, and a better reason probably could be found in the interfacial tension which exists at the gas-liquid-solid interface, which causes increased wetting of the carbon surface and greater retention of liquid at points of contact between adjacent rings.

The static holdups reported in this work with water solutions were obtained with rings which had been kept immersed in water when not in use. The static holdup for water on carbon rings, which was reported in Part I, was obtained by starting with dry rings and is about 25% lower than holdup in this part. Under normal conditions of use in a packed column, the static holdup would probably attain some intermediate value depending upon the relative humidity of the gas passing through the column.

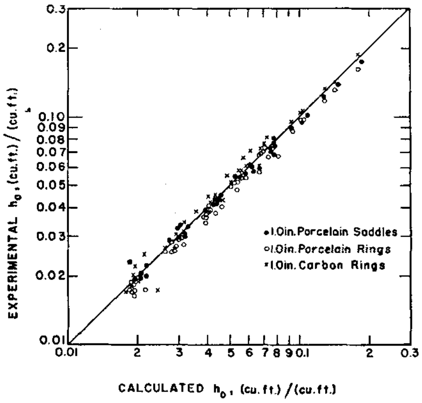

FIG. 9. COMPARISON OF EXPERIMENTAL AND CALCULATED OPERATING HOLDUPS.

APPLICATIONS

Estimation of Holdups. Although the equations tabulated in Table 2 were developed from data for one-inch packings, the good agreement as to the effects of the physical properties of the liquids with previous work on different packings makes it possible to estimate holdups for any packing for which water data are available. Extensive holdup data for six packings were reported in the first part of this study (4). Figures 13 to 16, inclusive, were prepared to supply factors to be applied to water holdups to correct for any departure from the viscosity, density, and surface tension of water at 20°C. To estimate the operating and static holdups for any liquid, at given liquid and gas rates, the corresponding water holdups are found first, as in Part I, and then multiplied by the three factors for viscosity, density, and surface tension as given in Figures 13 to 16.

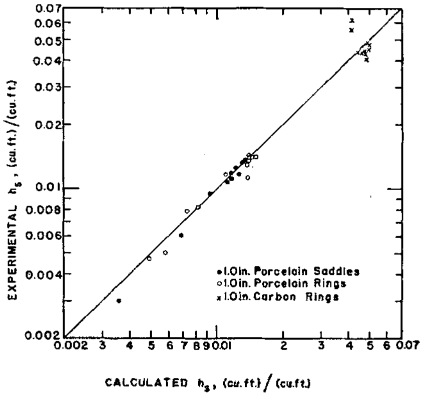

FIG. 10. COMPARISON OF EXPERIMENTAL AND CALCULATED STATIC HOLDUPS.

The use of these charts is equivalent to using the effects of the variables as given in Equations (1) to (5) in Table 2. Figures 9 and 10 show a comparison of the experimental points for water, water solutions, benzene, and methanol with values calculated from the charts or equations. It can be seen that there is good agreement between the two values.

Vaporization of Liquids in Packed Columns. In Parts I and II a design method was proposed for packed columns which consisted of determining the mass transfer coefficient, k_G, and the effective interfacial area, a, separately and combining the two to obtain the $k_G a$ required for design. The k_G is determined from the following equation:

$$\frac{k_G M_M P_{BM}}{G} = 1.195\left[\frac{D_P G}{\mu\,(1-\epsilon)}\right]^{-0.36}\left[\frac{\mu}{\rho D}\right]^{-0.67} \qquad (6)$$

It was pointed out in the introduction that Surosky and Dodge(*4*) vaporized water and several organic liquids in a column packed with 1.0-in. carbon rings and found $k_G a$ proportional to $D^{0.15}$ rather than $D^{0.67}$ as indicated by Equation(*6*). It may be possible to explain the difference if it can be shown that a is not the same for all liquids, as assumed by Surosky and Dodge(*4*) and other investigators. A comparison of the total holdups in 1.0-in. carbon rings for water, benzene, and methanol, which were three of the liquids employed, shows the organic liquids to have much greater holdups than water, as required to help explain the difference. To test this quantitatively Figure 11 shows a plot of $k_G a(\mu/\varrho D)^{2/3}$ vs. G at a liquid rate of 1,600 lb./(hr.)(sq.ft.) for the vaporization of these three liquids based on the data of Surosky and Dodge. If the 2/3 power on diffusivity held and the effective interfacial areas for the three liquids were the same, the data should fall on one line. It is obvious that this is not the case. If it is assumed that a is proportional to total holdup, h_t, and the effect of different total holdups on k_G is taken into account in the $(1-\varepsilon)$ term in Equation (6), then $k_G a(\mu/\varrho D)^{2/3}\ (h_t)\ (1-\varepsilon)^{0.36}$ plotted vs. G for the same data should bring the points in line. The results are shown in Figure 12, where it can be seen that the

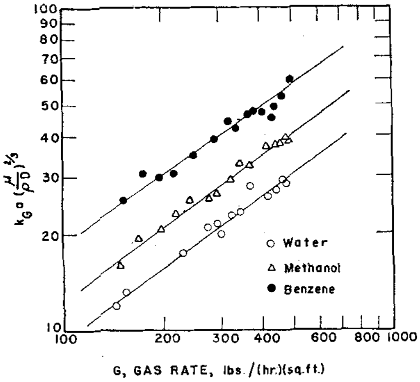

FIG. 11. VAPORIZATION MASS TRANSFER COEFFICIENTS FOR THREE SYSTEMS CORRECTED FOR DIFFUSIVITY.

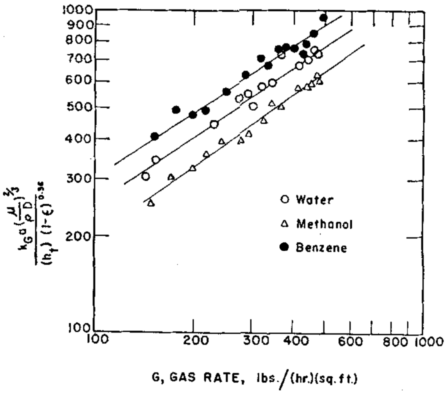

FIG. 12. VAPORIZATION MASS TRANSFER COEFFICIENTS FOR THREE SYSTEMS CORRECTED FOR DIFFUSIVITY AND HOLDUP.

points are in much better agreement than in Figure 11. There are several reasons that may be advanced to account for the disagreement that still exists. The total holdup may not be directly proportional to a or the proportionality constant may not be the same for all the liquids. In addition, the vaporization data may be in error because of the difficulties encountered in obtaining good data. The data used were obtained with a packing depth of 4.0 in.; corrections were made for end effects equivalent to 2.2 in., as found by experiment for water. Errors in measuring the packing depth or in assuming the same end effect for all liquids may easily account for some of the disagreement shown in Figure 12. If one had used the water vaporization data, and all the corrections suggested, it would have been possible to estimate the data for benzene and methanol vaporization within about 15% of the experimental values. Disagreement of this magnitude can be tolerated in the design of packed columns.

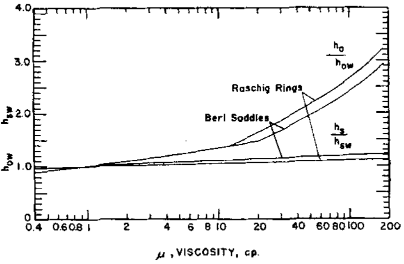

FIG. 13. FACTORS TO BE APPLIED TO WATER HOLDUPS TO ESTIMATE THE EFFECT OF VISCOSITY.

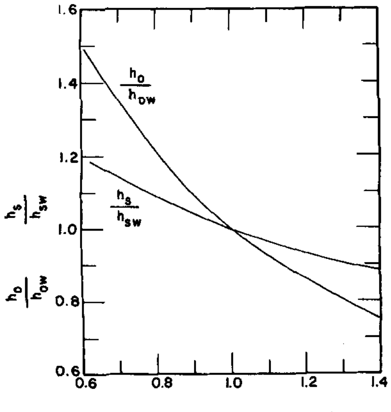

FIG. 14. FACTORS TO BE APPLIED TO WATER HOLDUPS TO DETERMINE THE EFFECT OF LIQUID DENSITY.

Estimation of a. Holdups can be of value in estimating both k_G and a for the purposes of determining the mass transfer coefficient, k_Ga, required for design. As was mentioned previously, the total holdup, h_t, which is the sum of the operating and static holdups, is required to evaluate the void fraction, ϵ, available for gas flow in the packing for use in Equation (6). This void fraction, ϵ, is simply the void fraction for the dry packing minus the total holdup, h_t.

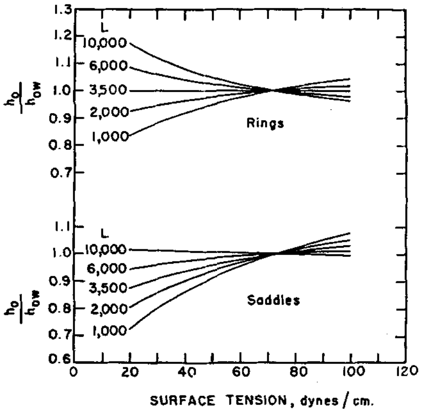

FIG. 15. FACTORS TO BE APPLIED TO WATER OPERATING HOLDUPS TO DETERMINE THE EFFECT OF SURFACE TENSION.

Total and operating holdups can be used to estimate effective interfacial areas for absorption and vaporization for any liquid from the areas presented in Part II for absorption in water. In absorption, a is proportional to operating holdup, and so it can be estimated as follows:

$$a_{abs} = (a_{abs})_w \frac{h_o}{h_{ow}} \tag{7}$$

The ratio h_o/h_{ow} is the product of the factors obtained from Figures 13, 14, and 15 which correct for liquid physical properties different from those of water.

In vaporization, a is proportional to total holdup, and the relationship

$$\frac{a_{vap}}{a_{abs}} = 0.85 \frac{h_t}{h_o} \tag{8}$$

which was found in Part I to hold for water, can be applied to estimate a_{vap} for any liquid from

$$a_{vap} = 0.85\,(a_{abs}) \frac{h_t}{h_o} \tag{9}$$

or

$$a_{vap} = 0.85\,(a_{abs})_w \frac{h_t}{h_{ow}} \tag{10}$$

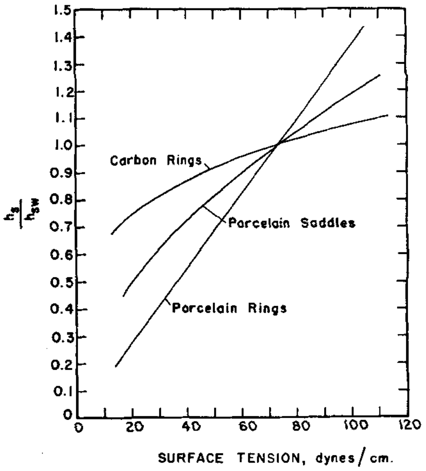

FIG. 16. FACTORS TO BE APPLIED TO WATER STATIC HOLDUPS TO DETERMINE THE EFFECT OF SURFACE TENSION.

The required values of $(a_{abs})_w$ and h_{ow} are available in Parts I and II for the common sizes of ring and saddle packings.

SUMMARY OF RESULTS AND CONCLUSIONS

Operating and static holdup data have been obtained for water solutions of sorbitol, calcium chloride, and a wetting agent as well as for benzene and methanol, by use of 1-in. porcelain and carbon rings and porcelain saddles.

Charts have been prepared for estimating holdups for any liquid from data available for water.

Applications of holdup data to explain the effect of diffusivity on the vaporization of liquids in packings and to estimate effective interfacial areas for mass transfer have been outlined.

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NOTATION

a = effective interfacial area, sq. ft./cu.ft.
c = constant in Equation (5)
D = diffusivity of solute in gas, sq. ft./hr.
D_p = diameter of sphere possessing the same surface area as a piece of packing, ft.
G = superficial gas rate, lb./(hr.) (sq.ft.)
h_o = operating holdup, cu.ft./cu.ft.
h_s = static holdup, cu.ft./cu.ft.
h_t = total holdup, cu.ft./cu.ft.
k_G = gas-phase mass transfer coefficient, lb. moles/(hr.) (sq. ft.) (atm.)
k_Ga = gas-phase mass transfer coefficient, lb. moles/(hr.) (cu. ft.) (atm.)
L = superficial liquid rate, lb./(hr.) (sq.ft.)
m = constant in Equation (5)
M_M = mean molecular weight of gas, lb./lb. mole
n = constant in Equation (5)
P_{BM} = mean partial pressure of inert gas in the gas phase, atm.

Greek Letters

μ = liquid viscosity, centipoises
= gas viscosity, lb./(hr.) (ft.)
ρ = liquid density, g./ml.
= gas density, lb./cu.ft.
σ = surface tension, dynes/cm.
ε = void fraction, cu. ft./cu.ft.

Subscripts

w = for water systems
abs = for absorption work without a chemical reaction
vap = for vaporization work

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CORRELATION OF DIFFUSION COEFFICIENTS IN DILUTE SOLUTIONS

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The diffusion coefficient is normally defined and assumed in this study to be the proportionality constant in the rate equation written for undirectional mass transfer as follows:

$$N_A = -D\frac{dC_A}{dz} \qquad (1)$$

Equation (1) is strictly applicable in ideal dilute solutions in which convective transport due to volume changes on mixing is negligible, and in which other possible modes of mass transfer are not operative. This paper represents an attempt to generalize the relation of D to conveniently available properties of dilute solutions so as to permit estimation of diffusion coefficients for engineering purposes.

PREVIOUS CORRELATION

In the earlier paper by Wilke (*10*) a method of correlating diffusion coefficients was proposed on the basis of qualitative conclusions of the Eyring theory(*3*) and the Stokes-Einstein relation. It was shown that the group $T/D\eta$, designated as the diffusion factor F, was essentially independent of temperature for available systems. Furthermore F could be represented as a smooth function of molal volume for diffusion of various solutes in a given solvent. In general it was assumed that this function extrapolated into the Stokes-Einstein equation at very large solute molal volumes.

DEVELOPMENT OF NEW CORRELATION

Sources of Data. At the time of the previous work so few data were available for diffusion of single solutes in a variety of solvents that the effect of solvent properties could not be brought into a general correlation. In a special effort to obtain suitable data of this kind a companion experimental study (*2*) was conducted involving the diffusion of iodine and toluene in a wide variety of hydrocarbon