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# A Unified Model for Countercurrent Vapor/Liquid Packed Columns. 2. Equations for the Mass-Transfer Coefficients, Mass-Transfer Area, the HETP, and the Dynamic Liquid Holdup

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In the preceding paper a model for the two-phase pressure drop in a packed column was derived from an analogy to electrical percolation on a conductor/insulator lattice. In this paper we extend that development to include the mass-transfer coefficients, the area available for mass transfer, the height of packing equivalent to a theoretical plate, and the dynamic liquid holdup.

## Introduction

In a preceding paper (Hanley et al., 1994) we developed a model for the two-phase pressure drop in a packed column by making an analogy to electrical percolation on a lattice composed of conductors and insulators. Additionally, we developed a new conceptual definition for flooding as the locus of vapor and liquid superficial velocities which causes a liquid cluster to form in the packing voids which spans the column diameter.

The analysis of the two-phase pressure drop presented in Hanley et al. (1994) is based upon an analogy between the behavior of the two-phase pressure drop and the electrical potential drop for a conductor/insulator mixture. In the electrical model of a percolation process, the conductors were replaced with insulators until the percolation threshold was reached. At this point, the network abruptly changed to nonconducting. Theory predicts that, near the percolation threshold, the potential drop (or pressure drop, if you will) should scale as

$$\left(\frac{\Delta p}{H}\right)_{2\phi} = \left(\frac{\Delta p}{H}\right)_{\text{wd}} \left\{1 - \frac{f}{f_c}\right\}^{-\alpha} \quad (1)$$

where  $f$  is the fraction of conductors replaced by non-conductors (or the fraction of liquid filled channels) and  $f_c$  is the incipient percolation threshold. We assumed that we could reexpress this relationship in the following terms:

$$\left(\frac{\Delta p}{H}\right)_{2\phi} = \left(\frac{\Delta p}{H}\right)_{\text{wd}} \left\{1 - \frac{C_L}{C_L^*}\right\}^{-\eta} \quad (2)$$

These two equations should be equivalent, so that

$$f = f_c \left\{1 - \left(1 - \frac{C_L}{C_L^*}\right)^\nu\right\} \quad (3)$$

where  $\nu = \eta/\alpha$ . The Wallis equation (Wallis, 1971) has been used to correlate the superficial liquid velocity at the incipient percolation threshold as a function of the vapor velocity and packing topology.

The fraction of voids occupied by the liquid,  $f$ , and the relative approach to the percolation threshold,  $f/f_c$ , play crucial roles in the developments below for the area available for mass transfer, the HETP, and the dynamic fractional liquid holdup. Equation 3 is thus important to keep in mind.

## Relations for the Mass-Transfer Coefficients

Generally speaking, both  $k_G$  and  $k_L$  are expected to increase with the "average" velocity of their respective

phases. It has often been assumed that the relevant "average" vapor velocity in the dimensionless correlations for  $k_G$  is simply the superficial vapor volumetric flux divided by the void fraction:

$$u_G = \frac{K_V(\rho_L/\rho_G)^{1/2}}{\epsilon} \quad (4)$$

This is strictly true only for a dry packing. As more and more vapor passages are choked off with liquid, the "average" vapor velocity through the remaining open channels must increase to keep the total mass flow constant. As the flood point is approached, fewer and fewer unobstructed vapor paths remain; the vapor velocity must increase explosively. In fact, it is relatively straightforward to show that

$$u_G = \frac{K_V(\rho_L/\rho_G)^{1/2}}{\epsilon(1 - f/f_c)^p} \quad (5)$$

where the scaling exponent  $p$  is expected to have a value close to the scaling exponent for the potential drop,  $\alpha$  (which we have been taking as equal to 2 for arrays of linear resistors). We consider the dimensionless scaling correlations for the vapor-phase mass-transfer coefficient,  $k_G$ , more nearly correct for packed columns when the vapor velocity above is used in place of the void fraction corrected superficial vapor volumetric flux traditionally employed.

On the other hand, the appropriate "average" liquid velocity is often taken to be

$$u_L = C_L/\epsilon \quad (6)$$

and would be much less affected by the onset of flooding because liquid can continue to flow into and out of the liquid-filled interstices and can also wet previously dry surface.

In what follows we will assume that the mass-transfer coefficients can be adequately correlated by the following expressions:

$$\frac{RTk_G d_e}{D_G} = A_G Re_G^{0.8} Sc_G^{1/3} \quad (7a)$$

$$\frac{k_L d_e}{D_L} = A_L Re_L^{1/2} Sc_L^{1/2} \quad (7b)$$

where

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$$Re_G = \frac{d_p K_V (\rho_L / \rho_G)^{1/2}}{\epsilon \mu_G (1 - f/f_c)^p} \quad (8a)$$

$$Sc_G = \frac{\mu_G}{\rho_G D_G} \quad (8b)$$

$$Re_L \approx \frac{4\delta u_L \rho_L}{\mu_L} \approx \frac{d_p C_L \rho_L}{\epsilon \mu_L} \quad (8c)$$

$$Sc_L = \frac{\mu_L}{\rho_L D_L} \quad (8d)$$

These particular power law correlations were chosen for convenience and for demonstration purposes only. The analysis presented below could be reformulated and performed with any liquid-phase and/or gas-phase mass transfer coefficient correlation(s) of interest. The only requirement would be that the definition for the gas-phase velocity be modified to agree with eq 8a.

### Area Available for Mass Transfer

The surface area available for mass transfer is tied up in a complex way with the magnitudes of the individual mass-transfer coefficients and with the structure of the liquid-containing clusters within the voids of the packing. It has been argued that the liquid-filled void spaces allow for the passage of very little vapor. As the flood point is approached, more and more of the packing surface covered with a liquid film becomes "shielded" or in some cases surrounded by these liquid-filled interstices. We anticipate that the "shielded" area is closely related to the total "perimeter" for liquid clusters (the number of empty neighbors *inside and around* a cluster is called its perimeter). However, we will not pursue this point here. Figure 1 is an illustration of how clustering of the locally flooded void spaces can "shield" or surround wetted surface area. The void spaces marked with a "B" (for "blocked") will experience very little in the way of gas flow. In other words, the gas phase is relatively "stagnant" in those voids which are "shielded" or surrounded by liquid-filled voidages. In terms of mass transfer, this "shielding" phenomenon will make little difference for systems which are strongly dominated by the resistance of the liquid film; the fact that the gas phase is relatively "stagnant" in some spots around the column is unimportant because it is the liquid film which limits the rate of mass transfer irrespective of the state of the gas phase above it. On the other hand, the "shielding" effect is extremely important for systems which are strongly gas phase controlled. In this case, the mass transfer is virtually eliminated on the wetted surfaces "shielded" by the locally flooded voids in comparison to that taking place on the wetted surface experiencing the full flow rate of the gas phase. When the gas phase and liquid phase offer comparable resistances to mass transfer away from hydraulic flooding, then essentially two "parallel" modes of mass transfer are possible as one approaches the flood point—in the shielded regions there will be a value for  $K_{OG}$  weighted more heavily by the gas-phase resistance, while in the channels open to gas flow there will be another value for  $K_{OG}$  more heavily weighted by the liquid-phase resistance. For this reason, we will consider two limiting cases only: (i) a system in which there is only a liquid-phase resistance and (ii) a system which is dominated by the gas-phase resistance far from flooding. Intermediate situations turn out to be quite complex and will not be considered here.

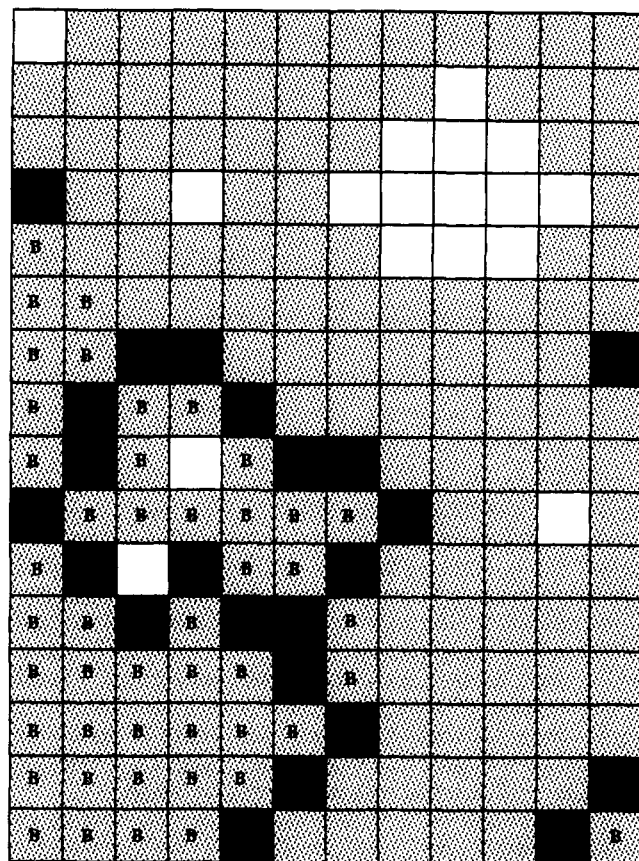


Figure 1. Schematic of the different "types" of area in a packed column. The white areas represent dry spots in the column. The blackened areas represent locally flooded voids. The shaded areas correspond to wetted surface; those marked with a "B" depict wetted surface which is blocked.

Since there are void spaces in the packing which are filled with liquid, the surface area per unit volume of the packing is reduced. The amount of surface area per unit volume *open* at any set of flow conditions is given by the difference between the total open area and the fraction of the total open area choked off by liquid:

$$a_{\text{open}} = (1 - f)a \quad (9)$$

Unfortunately, the open surface area of the packing is not necessarily equal to the vapor/liquid interfacial area participating in mass transfer. As others have noted, there are many "kinds" of area in a packed column (Weisman and Bonilla, 1950; Shi and Mersmann, 1985). Some of the more important ones would be

I. "dry" packing surface area:  $a_d$

II. "wetted" area

A. participating in mass transfer:  $\hat{a}_m$

1. "wetted" packing surface area "open" to gas flow:  $a_{ow}$
2. "wetted" packing surface "blocked" to gas flow:  $a_{bw}$  (case i analysis)
3. other surface involved in mass transfer (liquid spray, bubbles, etc.):  $a_e$

B. not participating in mass transfer

1. liquid-filled interstices:  $f_a$
2. "blocked" wetted area:  $a_{bw}$  (case ii analysis)

The following equations relate the various types of specific surface area:

$$a = a_d + a_{ow} + fa + a_{bw} \quad (10a)$$

$$a_{ws} = a_{ow} + a_{bw} \quad (10b)$$

$$a_{open} = (1-f)a = a_d + a_{ow} + a_{bw} \quad (10c)$$

$$\hat{a}_m = a_{ow} + a_{bw} + a_e \approx a_{ow} + a_{bw} (=a_{ws}) \quad (\text{case i}) \quad (10d)$$

$$\hat{a}_m = a_{ow} + a_e \approx a_{ow} \quad (\text{case ii}) \quad (10e)$$

From the above relations, we find that

$$\hat{a}_m \approx (1-f)a - a_d \quad (\text{case i}) \quad (11a)$$

$$\hat{a}_m \approx (1-f)a - a_d - a_{bw} \quad (\text{case ii}) \quad (11b)$$

Clearly the above equations are a simplification of the reality of packed column operation. Any attempt to derive general expressions for the relative proportions of dry and wetted area is complicated by the effects of liquid maldistribution, by the changes in this distribution as the liquid flows down the packing, and by the fact that localized "flooding" is superimposed upon the wetting process. Unfortunately there is a lack of experimental data related to the wetting of a packing under known conditions of liquid maldistribution. Thus, the analysis below is conjectural but very much in keeping with the available experimental observations and common sense.

In the absence of any definitive theory on wetting in packed columns, let us assume that the wetting process and the process leading to the choking off of voids with liquid are independent and that  $a_d$  can be well described by a stretched exponential function of the superficial liquid Weber number:

$$a_d = (1-f)a \exp(-\Psi We_L^z) \quad (12)$$

where

$$We_L = \frac{d_e C_L^2 \rho_L}{\epsilon \sigma_L} \quad (13)$$

The Weber number has been found to be the most significant dimensionless group containing a liquid flow rate in many studies of the wetted area of packed columns (Onda, 1967; Puranik and Vogelpohl, 1974; Kolev, 1976; Zech and Mersmann, 1978). The stretched exponential form guarantees that  $a_d = a$  when there is no liquid flow, and it presumes that all of the available surface area will be wet for sufficiently high liquid Weber numbers. Stretched exponentials have been found to be sufficiently flexible to describe many types of phenomena involving an "exponential-like" decay (Phillies, 1986). Of course, there may be situations in which a certain amount of packing surface area always remains "dry", for example contamination of the surface with an essentially "unwettable" material (Chen and Chuang, 1989), but we will ignore this complication. The fundamental interaction parameters governing the wetting process, such as the interfacial tension and the advancing and receding contact angles, have been lumped into the parameter  $\Psi$ . The form above presumes that, for a given system and packing, wetting is dominated by liquid flow and that vapor flow has only a minor effect. Mayo et al. (1935) measured the wetted area or random ring packings and found that air flow had no effect on the wetted area until the flood point was reached. Yoshida and Koyanagi (1962) came to a similar conclusion. There is some evidence that countercurrent

vapor flow can affect the amount of area which is wetted (Shulman et al., 1955), but the effect is relatively minor and we ignore it as a first approximation. We must stress, however, that there has been little verification of the validity of the dimensionless groups usually reported as important. In particular, studies of wetting in packed columns have, for the most part, focused upon the liquid and vapor flow rate effects and liquid physical property effects; very little effort has been put forth to study the pertinence of the proposed dimensionless groups with regard to the effect of a packing's "equivalent diameter". We will discuss this point further in a later section.

As the flood point is approached, more and more of the wetted surface becomes blocked to gas flow because it is "shielded" or in some cases surrounded by liquid-filled interstices. We will postulate that a certain fraction of the total wetted area is unavailable for mass transfer in case ii and that this fraction increases as a power of  $(f/f_c)$ :

$$a_{bw} = \left(\frac{f}{f_c}\right)^n (1-f)a \{1 - \exp(-\Psi We_L^z)\} \quad (\text{case ii}) \quad (14)$$

The resulting expressions for the area available for mass transfer are

$$\hat{a}_m \approx (1-f)a \{1 - \exp(-\Psi We_L^z)\} \quad (\text{case i}) \quad (15a)$$

$$\hat{a}_m \approx \left(1 - \left(\frac{f}{f_c}\right)^n\right) (1-f)a \{1 - \exp(-\Psi We_L^z)\} \quad (\text{case ii}) \quad (15b)$$

It is valuable to note that the expressions proposed above for the wetted surface area are somewhat reminiscent of the equation of Onda (1967) for the wet surface area:

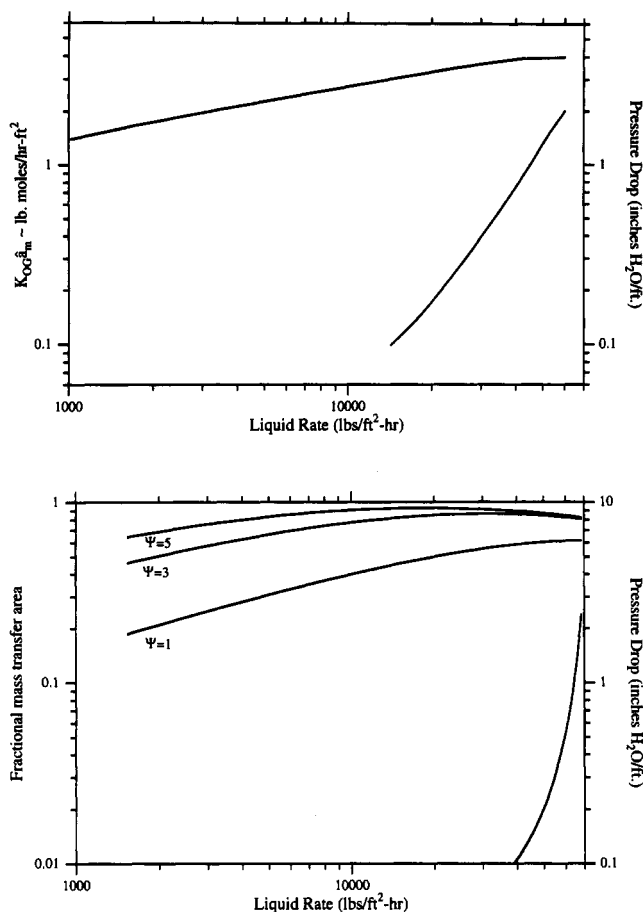
$$\frac{a_{wet}}{a} = 1 - \exp \left[ -1.45 \left( \frac{\sigma_L}{\sigma_c} \right)^{3/4} Re_L^{0.1} Fr_L^{-0.05} We_L^{0.2} \right] \quad (16)$$

where  $Fr_L$  is the Froude number of the liquid,  $Re_L$  is the liquid Reynolds number, and  $\sigma_c$  is a "critical" surface tension for the packing material under investigation. Indeed, Onda's equation might be used to advantage in the above formulation since its explicitly accounts for liquid/surface interaction effects albeit in an *ad hoc* way. A McLaurin expansion of Onda's equation gives

$$\frac{a_{wet}}{a} \approx 1.45 \left( \frac{\sigma_L}{\sigma_c} \right)^{3/4} Re_L^{0.1} Fr_L^{-0.05} We_L^{0.2} + \dots \quad (17)$$

This truncated McLaurin expansion yields, to first order, a "power law" for the wetted area which is very similar to other empirical power law relationships found in the literature. These types of experimentally derived correlations might be useful for extending the applicability of percolation model developed here until such time that wetting in packed columns is more thoroughly understood.

One common method for experimentally measuring the mass-transfer area for systems in which the liquid film is the dominant resistance is by  $CO_2$  absorption into mild caustic (Leva, 1955; Eckert, 1963). The data are most often reported in terms of  $K_{OG} \hat{a}_m$  because the concentration gradient in the liquid is unknown. Normally,  $K_{OG} \hat{a}_m$  is proportional to the rate of  $CO_2$  absorption, which itself is proportional to the mass-transfer area. Eckert (1963) presents a plot for data taken in this way up to flooding ( $\sim 2.5$  in.  $H_2O/ft$ ) for 2-in metal Pall rings. In our previous paper (Hanley et al., 1994) we examined the pressure drop for air/isopar with 2-in. Pall rings. Using parameters



**Figure 2.** Calculated behavior of the mass-transfer area for the absorption of CO<sub>2</sub> into mild caustic as a function of the packing wettability parameter,  $\Psi$ , along with the data of Eckert. Since the mass transfer is "liquid phase controlled" there is no loss of wetted area by "shielding".

derived from these data, we have calculated the mass-transfer area up to flooding for CO<sub>2</sub> absorption into mild caustic as a function of the wettability parameter,  $\Psi$ . These calculations are shown in Figure 2 along with our estimation of the pressure drop. The shapes for the mass-transfer areas predicted by our model are in very good agreement with the shape of Eckert's measured data. In addition, the estimates of the flood point are in very good agreement. Our pressure drop is different from Eckert's, but our prediction is based on Nutter's reported data for air/isopar (Nutter, 1987), not on Eckert's own data. Keep in mind that the mass-transfer area calculated here is valid only for a system in which the liquid resistance is dominant. The mass-transfer area calculated via the CO<sub>2</sub> absorption method is not necessarily appropriate under other circumstances, such as gas-side control of the mass transfer.

Much of the data in the literature pertaining to the effective interfacial area for mass transfer were obtained by measuring the rate of mass transfer and dividing out an assumed overall mass-transfer coefficient. This method should work reasonably well under two conditions: either (1) one is far from the flood point for either a gas-phase-controlled or liquid-phase-controlled mass-transfer system, or (2) one is dealing with a liquid-phase-controlled mass-transfer process all the way to the flood point. Either of these two conditions must be fulfilled because of the percolation-induced increase in the gas-phase mass-transfer coefficient described earlier. If one neglects this effect when dividing out the overall mass-transfer coefficient, a percolation term gets "left behind", making it appear as though the effective interfacial area increases

as one approaches flooding, rather than decreasing as predicted earlier. It is easy to show that neglect of the percolation induced acceleration of the gas-phase mass-transfer coefficient leads to the following approximate expression for the effective interfacial area when the mass transfer is gas phase controlled:

$$\hat{a}_{m\text{-app}} \approx \frac{\hat{a}_m}{(1 - f/f_c)^{1.6}} \quad (18)$$

The factor in the denominator has its origins in the gas-phase mass-transfer coefficient. The exponent of 1.6 is the product of the universal scaling exponent,  $\alpha$ , with the power law exponent on the gas Reynolds number in the expression for the gas-phase mass-transfer coefficient (usually taken to be 0.8). While we do not deny that some area is created as the macroscopic flood point is approached (see eqs 10d and 10e), the loss of area due to localized flooding (which is always neglected in other models), along with the loss due to "unavailability", far exceeds it.

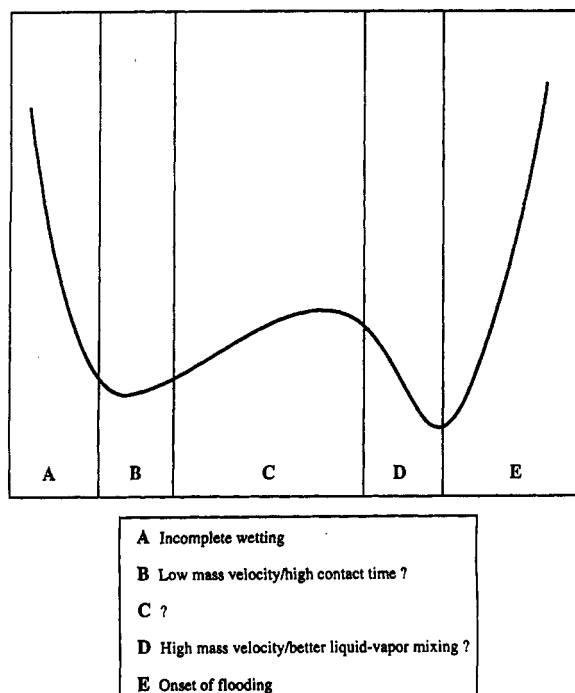
### Behavior of the HETP

The notion of a depth of packing equivalent in its separation capacity to a theoretical plate in a trayed distillation column, commonly referred to as the height of a theoretical plate or the HETP, is often used as a measure of packing performance. While there are a number of pitfalls associated with the application of this concept, it is a well-accepted and widely used quantity. It often allows the design engineer to estimate quickly the height of a packed column necessary to equal the separation performance of a given trayed column or vice versa; this type of information is necessary for the initial economic decision of whether to choose a packed or trayed column to perform a given separation. Of course, other factors, such as acceptable pressure drop and turn-up or turn-down capacity also enter into the decision.

While the general features displayed by the pressure drop and the liquid holdup are the same in all packed columns, the behavior of the HETP is more enigmatic. Murch describes five different regimes for a plot of HETP versus superficial vapor volumetric flux at fixed  $L/V$  (Murch, 1953). However, Murch explicitly states that all five regimes are not necessarily found for all types and sizes of packings. Figure 3 is a schematic of HETP versus superficial vapor volumetric flux at fixed  $L/V$  showing the regimes described by Murch along with his proposed explanations for their occurrence. Billet (1967) observed a number of distinct shapes for the HETP versus superficial vapor volumetric flux for metal pall rings; Murch's five regimes were not always found. Bravo et al. (1985) found that the HETP monotonically increases with increasing  $K_V$  over a wide range for gauze structured packings. Chen and Chuang (1989) have reported HETP data for structured packings of three different designs under a variety of test conditions. There does not appear to be any consistent trend in their HETP data with  $K_V$ . Certainly other examples could be cited to demonstrate that the variation of the HETP with  $K_V$  is apparently erratic.

The seeming unpredictability of the HETP leads to a fair amount of error in the estimation of the mass-transfer efficiency of a given column under operating conditions different from the nominal or away from conditions tested in small-scale laboratory or pilot plant runs. In addition,





**Figure 3.** HETP regimes identified by Murch (1953) and proposed explanations for their appearance.

“scale-up” or “scale-down” of efficiency data from a packing of given dimensions to a topologically similar packing of different dimensions is tenuous. A better understanding of the HETP is clearly necessary.

It turns out that the percolation model for the area available for mass transfer and for the vapor-phase mass-transfer coefficient can be used to explain most of the observed variations in HETP with  $K_V$ . The particular shape assumed by a curve of HETP versus  $K_V$  at fixed  $L/V$  depends upon subtle balances among the wettability of the packing, the relative magnitudes of the vapor-phase and liquid-phase mass-transfer coefficients away from the flood point, and the rate of area loss near the flood point relative to the rate of increase in the overall mass-transfer coefficient,  $K_{OG}$ , near flooding.

The HETP is given approximately by

$$\text{HETP} = \left( \frac{G_{Gm}}{K_{OG} \hat{a}_m P} \right) \frac{\ln(\lambda)}{\lambda - 1} \quad (19)$$

where

$$\lambda = \tilde{m} G_{Gm} / G_{Lm} \quad (20)$$

$$\frac{1}{K_{OG}} = \frac{1}{k_G} + \frac{\tilde{H}}{k_L} \quad (21)$$

and  $\tilde{H}$  is the Henry's law constant (or an apparent Henry's law constant over a limited range of composition) in the equilibrium relationship

$$\frac{\partial(y_i P)}{\partial c_i} = \tilde{H} \quad (22)$$

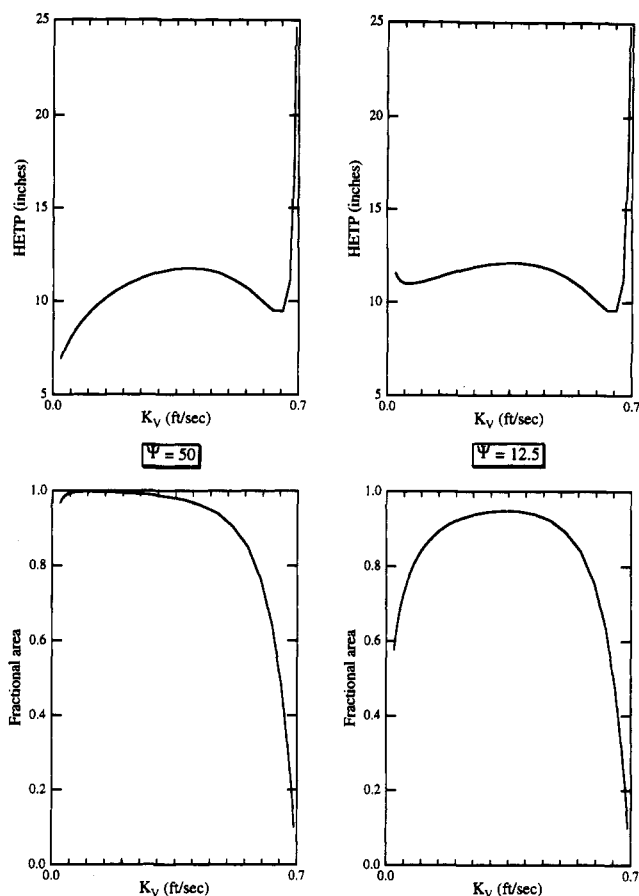
“ $\tilde{m}$ ” is related to “ $\tilde{H}$ ” in the following way:

$$\tilde{m} = \frac{\tilde{H} \rho_L}{P M_L} \quad (23)$$

$G_{Gm}$  is the molal velocity of the vapor phase and  $G_{Lm}$  the molal velocity of the liquid phase.

A rich and varied assortment of HETP shapes are possible because of the potentially divergent behaviors of  $K_{OG}$  and  $\hat{a}_m$  as the flood point is approached in systems dominated by the gas-phase resistance far from flooding (case ii). To illustrate this point, let us consider only the case of fixed  $L/V$ . For constant  $L/V$ , the individual mass-transfer coefficients making up  $K_{OG}$  increase with increasing vapor (liquid) mass flux through the voids while  $\hat{a}_m$  first increases with vapor flux and then begins to decrease as the flood point is approached. Under certain circumstances the abrupt increase in the vapor-phase mass-transfer coefficient due to the reduction in open flow paths begins to occur at approximately the same point as the decrease in mass-transfer area begins. The explosive rise in  $K_{OG}$  dominates the initial loss of mass-transfer area so that the HETP dips downward on first approach to the flood point. Even closer to flooding, however,  $K_{OG}$  can become increasingly dominated by the liquid-phase mass-transfer coefficient, if it is of the right order of magnitude. This deceleration in the rate of increase of the slope of  $K_{OG}$  versus  $K_V$  reverses the situation described earlier—loss of mass-transfer area begins to dominate the effects of the increasing overall mass-transfer coefficient and the HETP now begins to rise—the onset of “mass-transfer flooding”. Thus, the pocket in HETP at high flow rates (regimes D and E in Murch's scheme; see Figure 3) is determined by a delicate balance between the magnitudes of the liquid-phase and vapor-phase mass-transfer coefficients on the one hand and the wetting/flooding of available surface area on the other. However, the behavior just described is not always the case; it depends sensitively upon the relative magnitudes of the gas-phase and liquid-phase resistances as well as upon the relative rate of increase in the overall mass-transfer coefficient compared to the rate of loss of mass-transfer area. In short, the divergence of the HETP near flooding is not always predicted—the HETP can diverge near flooding, stay nearly the same, or under some extraordinary conditions decrease.

Figures 4 and 5 illustrate a few of the HETP “shapes” possible when the vapor-phase mass-transfer coefficient,  $k_G$ , is initially “controlling”. The curves were generated by varying the parameter  $\Psi$ , which controls the wettability of the packing. The front factor for the  $k_G$  correlation,  $A_G$ , was fixed at 0.075;  $A_L$  was fixed at 15. These values were selected for illustration purposes only; they were chosen so that the “pocket” in the HETP near flooding would be present. Thermodynamic and transport properties were taken to be “typical” values for the binary system *o*-xylene/*p*-xylene at 100 Torr and 78.33 °C. The other parameters used in generating this figure are listed in Table 1. The packing was assumed to have a specific surface area of 200 m<sup>2</sup>/m<sup>3</sup> and a void fraction of  $\epsilon = 0.75$ .  $\Omega$  and  $m$  were assumed to be unity. For  $\Psi = 50$  the packing surface is essentially completely wet even for low loadings. Under these conditions the HETP curve away from the flood point looks like what would be expected if the mass-transfer area in eq 19 were held constant. For the case  $\Psi = 12.5$  we begin to see the signature of incomplete wetting of the packing surface; there is a distinct upturn in the HETP at low loadings. When  $\Psi = 7$  there is a more pronounced upturn in the HETP at low loadings followed by a distinct “plateau” where the HETP does not vary significantly. This type of behavior is commonly found in the literature on distillation in packed towers. Finally, when the packing surface is not wetted well at all, illustrated when  $\Psi = 3$ , the HETP decreases monotonically



**Figure 4.** Variation of the HETP with  $K_V$  at total reflux and with the packing "wettability" parameter,  $\Psi$ , for a system which is gas phase controlled. Other parameters used in constructing these curves are reported in Table 1.

with an increased loading all the way to the flood point. Shapes similar to this are also often found in the literature on distillation.

Figure 6 illustrates the predicted behavior of the HETP when the mass transfer is completely controlled by the liquid film resistance as a function of the packing wettability parameter,  $\Psi$ ;  $A_L$  was fixed at 10. It should be apparent from this plot and the prior two that the pocket in the HETP observed near flooding is a sign that the mass transfer is vapor phase controlled.

### Calculation of the Dynamic Fractional Liquid Holdup

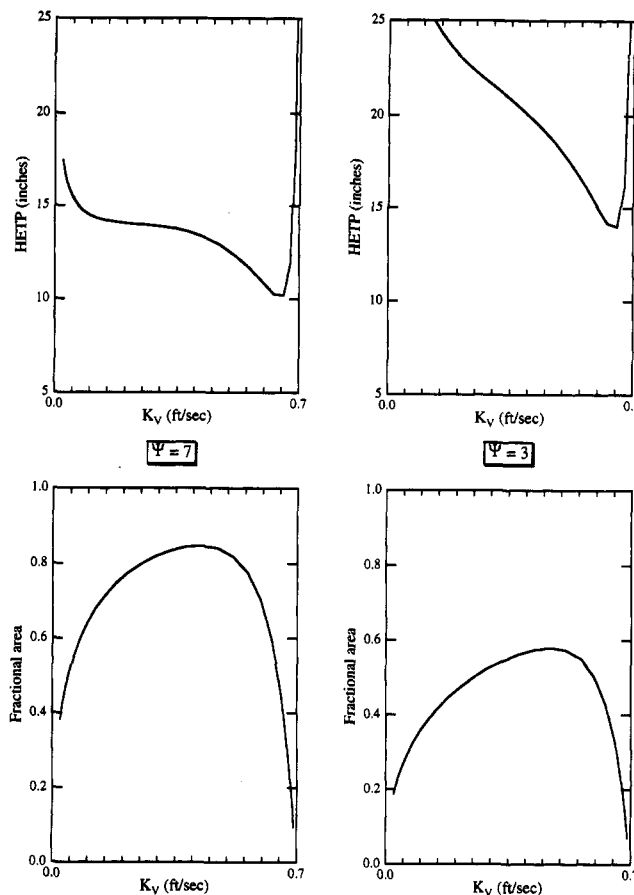
In the packing,  $f$  corresponds to the fraction of pores, or cells, which are liquid filled. If we assume that there are  $N$  cells, each with a volume,  $V_{\text{cell}}$ , then the liquid-filled cells hold a liquid inventory of

$$NV_{\text{cell}}f \quad (24)$$

Many of the other voids in the packed column, which still "conduct", are not empty of liquid, however. If these wetted cells are each coated with a film of thickness,  $\delta$ , then they contribute

$$NV_{\text{cell}}(1-f)\{1 - \exp(-\Psi We_L^2)\}a\delta \quad (25)$$

The total dynamic fractional holdup,  $h$ , is thus given by the sum of these two expressions, divided by the product



**Figure 5.** Variation of the HETP with  $K_V$  at total reflux and with the packing "wettability" parameter,  $\Psi$ , for a system which is gas phase controlled. Other parameters used in constructing these curves are reported in Table 1.

**Table 1<sup>a</sup>**

$P = 0.1316 \text{ atm}$		$H = 15 \text{ atm cm}^3/\text{mol}$
$T = 78.33 \text{ }^\circ\text{C}$		$M = 106 \text{ g/mol}$
vapor properties	liquid properties	misc coeff
$\rho_G = 5.609 \times 10^{-4}$	$\rho_L = 0.8157$	$f_c = 0.25$
$\mu_G = 7.400 \times 10^{-5}$	$\mu_L = 0.0037$	$z = 1/4$
$D_G = 0.19$	$D_L = 3.9 \times 10^{-5}$	$\nu = 1$
	$\sigma_L = 22$	$\eta = 2$
		$p = 2$

<sup>a</sup> All nondimensionless quantities are reported here in cgs units.

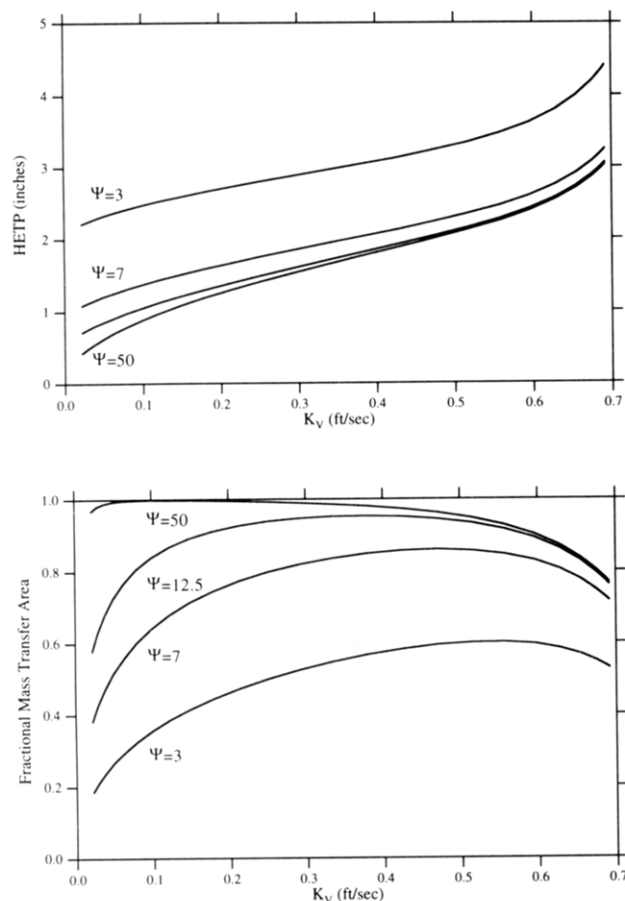
of  $N$  and  $V_{\text{cell}}$  (this is the total volume of the void space in the column):

$$h = f + (1-f)\{1 - \exp(-\Psi We_L^2)\}a\delta \quad (26)$$

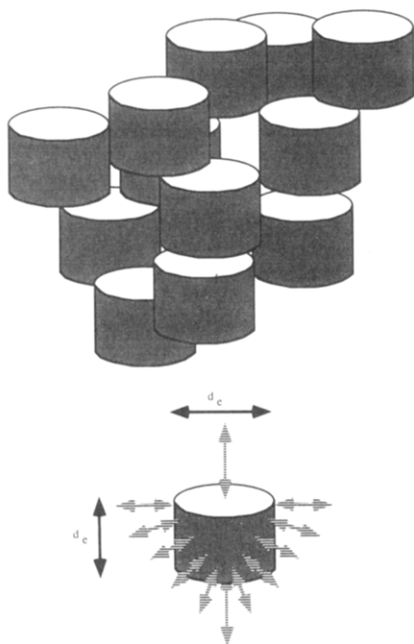
In order to calculate an approximation to the film thickness,  $\delta$ , coating the open cells, we will first assume that there is an average amount of open area and of dry area at any point in the column bed (which is independent of vertical displacement in the packing). For a completely dry packing, the average open area is assumed to be  $\pi R^2 \epsilon$ , where  $R$  is the radius of the column.

Let us consider the voids open to gas flow to form a number of short, interconnected straight tubes of diameter and of length  $d_e$ , as displayed in Figure 7. We further assume that the liquid flow is divided equally among those tubes at the surface of the packing which are not flooded and which are not dry:

$$q_L = Q_L / \langle n_w \rangle \quad (27)$$

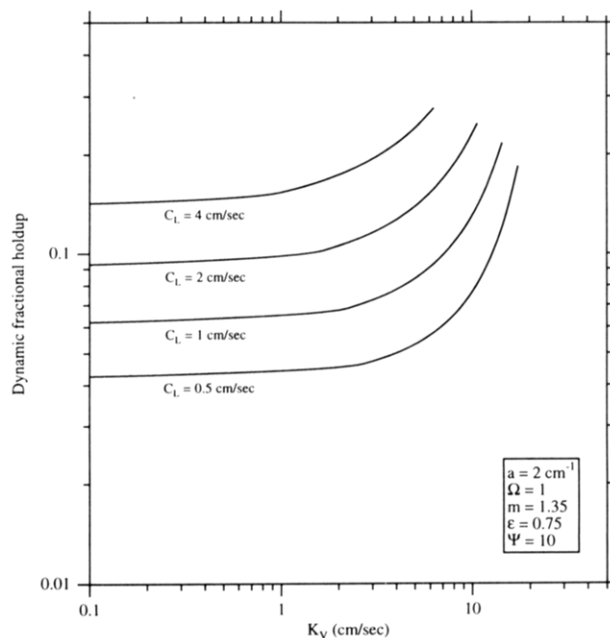


**Figure 6.** Variation of the HETP with  $K_V$  at total reflux and with the packing "wettability" parameter,  $\Psi$ , for a system which is liquid phase controlled. Other parameters used in constructing these curves are reported in Table 1.



**Figure 7.** Depiction of the packed column interstices as short, interconnected channels of characteristic dimension  $d_e$ . Vapor and liquid can enter or leave an element from virtually any direction.

where  $Q_L$  is the total volumetric flow rate of liquid supplied to the packing,  $q_L$  is the volumetric flow rate of liquid in a wetted tube, and  $\langle n_w \rangle$  is the number of wetted tubes. It is clear that for a totally dry column the total area of all of the tubes must equal the average open cross sectional



**Figure 8.** Calculated variation of the dynamic fractional liquid holdup with the density-corrected superficial vapor velocity for various fixed values of the superficial liquid velocity. The data in Table 1 were used for physical and thermodynamic properties. Otherwise, parameter values are found in the figure.

area of the column:

$$\pi(d_e^2/4)\langle n_T \rangle = \pi R^2 \epsilon \quad (28)$$

The following condition must also hold, based upon our previous calculation of the wetted area:

$$\langle n_w \rangle = \langle n_T \rangle (1 - f) \{1 - \exp(-\Psi We_L^z)\} \quad (29)$$

Thus

$$q_L = \left( \frac{Q_L}{\pi R^2} \right) \left( \frac{\pi d_e^2}{4\epsilon(1-f)\{1 - \exp(-\Psi We_L^z)\}} \right) = \frac{\pi d_e^2 C_L}{4\epsilon(1-f)\{1 - \exp(-\Psi We_L^z)\}} \quad (30)$$

If we apply Nusselt's formula for the thickness of a laminar film flowing down a flat plate (assuming that  $\delta \ll d_e$ ):

$$\delta = \left( \frac{3\mu_L C_L d_e}{4(1-f)\rho_L g \epsilon \{1 - \exp(-\Psi We_L^z)\}} \right)^{1/3} \quad (31)$$

Combining the above results:

$$h = f + (1 - f)^{2/3} \{1 - \exp(-\Psi We_L^z)\}^{2/3} \left( \frac{3\mu_L C_L d_e}{4\rho_L g \epsilon} \right)^{1/3} a \quad (32)$$

Figure 8 is a plot showing the calculated variation of the dynamic fractional holdup with superficial vapor velocity, with the superficial liquid velocity as a parameter. The values of the coefficients used in the construction of the plot are given in the figure and in Table 1. The magnitudes of the liquid holdups as well as the overall shapes of the holdup curves are in good agreement with fractional holdup data found in the literature (for example, see Shulman et al. (1955a,c)).



The Nusselt expression for the thickness of the liquid film is clearly a simplification. The expression for the liquid holdup can be modified as more is understood about the thickness of a liquid film in contact with a turbulent, countercurrent, vapor stream.

## Conclusions

Models for the mass-transfer coefficients, the mass-transfer area, the HETP, and the dynamic liquid holdup have been derived from percolation ideas. The models all involve the same definition for the flood point developed in the percolation model for the pressure drop—formation of a liquid cluster spanning the column diameter—and do not necessitate the introduction of concepts such as the “mass-transfer flood point”. In addition, the models involve many of the same parameters which relate to flood point and to packing wettability.

The equations developed here predict that the relative magnitudes of the mass-transfer coefficients are intimately connected to the definition of mass-transfer area. Characterization of the mass-transfer area by experimental methods in which the relative magnitudes of the liquid- and vapor-phase mass-transfer coefficients are different from the actual system of interest can lead to errors. A particular example of this is the use of CO<sub>2</sub> absorption data into mild caustic (liquid-phase controlled) to measure the mass-transfer area; this mass-transfer area is not appropriate in gas-phase-controlled systems.

In addition, the percolation models for the mass-transfer area and individual mass-transfer coefficients can explain the observed shapes and magnitudes of the HETP. In particular, the pocket in the HETP often observed near loading (at fixed  $L/V$ ) occurs in gas-phase-controlled systems only because of the competition between a rapidly increasing gas-phase mass-transfer coefficient and a decreasing amount of area available for mass transfer due to mass-transfer-area “shielding”.

The shapes for the dynamic liquid holdup curves are also well-described by the percolation model. The dynamic holdup has two contributions: (i) that from the local flooded voidages and (ii) the liquid spread as a film on the packing. The second term is most important far from flooding while the first term is relatively unimportant until loading.

Future work in this area should be focused in a number of areas. These include but are not limited to (1) understanding the flooding and liquid cluster formation behavior of packings; (2) understanding the variation of dry surface in the column with liquid and vapor flow rate as well as with surface wettability, characterized by advancing and/or receding contact angles, for example; (3) understanding the “nonuniversal” behavior of packed columns, for example, how the front factors on the pressure drop equations and mass-transfer coefficient correlations are related to the topological structure of the packing; and (4) the thickness and mass-transfer behavior of well-formed liquid films and of rivulets in random packing media in which there is a turbulent gas flow. Much work still remains to be done before a quantitative model for all aspects of packed column behavior can be claimed.

## Nomenclature

$a$  = total specific surface area of packing  
 $a_d$  = dry specific surface area  
 $a_s$  = specific surface area involved in mass transfer not coming from the packing surface (e.g., droplets)  
 $a_m$  = specific surface area available for mass transfer

$a_{\text{open}}$  = “open” specific surface area, that which is not locally “flooded”  
 $a_{\text{bw}}$  = “blocked” wetted specific surface area  
 $a_{\text{ow}}$  = wetted specific surface area participating in mass transfer which is “open” to gas flow  
 $a_{\text{ws}}$  = wetted specific surface area  
 $A_G$  = front factor for the dimensionless  $k_G$  correlation  
 $A_L$  = front factor for the dimensionless  $k_L$  correlation  
 $C_L$  = superficial liquid volumetric flux based upon the empty tower cross section  $L/\rho_L\pi R^2$   
 $C_L^*$  = superficial liquid velocity at the macroscopic flood point when the density-corrected superficial vapor velocity is  $K_V$   
 $d$  = spatial dimension; diameter of spherical packing unit  
 $D$  = column diameter  
 $d_e$  = channel equivalent diameter  
 $D_G$  = gas-phase diffusion coefficient  
 $D_L$  = liquid-phase diffusion coefficient  
 $f$  = fraction of cells occupied  
 $f_c$  = fraction of cells occupied at the percolation threshold  
 $Fr_L$  = liquid Froude number  
 $g$  = gravitational acceleration  
 $g_{\text{eff}}$  = effective gravitational acceleration =  $g \sin(\vartheta)$   
 $G$  = mass flux of gas based on the empty tower cross section =  $V/\pi R^2$   
 $G_{\text{Gm}}$  = molar flow rate of the vapor phase  
 $G_{\text{Lm}}$  = molar flow rate of the liquid phase  
 $\bar{H}$  = Henry's law constant in the equation  $p_i = \bar{H}c_i$   
HETP = height of packing equivalent to a theoretical plate  
 $k_G$  = gas-phase mass-transfer coefficient  
 $k_L$  = liquid-phase mass-transfer coefficient  
 $K_{OG}$  = overall mass-transfer coefficient  
 $K_V$  = density-corrected superficial vapor volumetric flux based on the empty tower cross section =  $G/(\rho_L - \rho_G)\rho_G^{1/2} \sim G/(\rho_L\rho_G)^{1/2}$   
 $L$  = mass flow rate of the liquid phase  
 $m$  = constant in the Wallis flooding equation  
 $\bar{m}$  = Henry's law constant in the equation  $y_i = \bar{m}x_i$   
 $M_L$  = average molecular weight of the liquid phase  
 $n$  = exponent for the amount of blocked wetted surface for a fractional approach to macroscopic flooding of  $f/f_c$   
 $N$  = number of packing “cells” for liquid and vapor flow  
 $\langle n_T \rangle$  = total number of “cells” of characteristic dimension  $d_e$  in the packing  
 $\langle n_W \rangle$  = number of packing “cells” wetted by the liquid  
 $P$  = column pressure  
 $(\Delta p/H)_{2\phi}$  = two-phase pressure drop  
 $(\Delta p/H)_{\text{wd}}$  = wetted/draind pressure drop  
 $q_L$  = volumetric flow rate of liquid in a packing “cell” of equivalent diameter  $d_e$   
 $Q_L$  = total volumetric flow rate of liquid supplied to the packing  
 $R$  = gas constant; column radius  
 $Re_G$  = gas-phase Reynolds number  
 $Re_L$  = liquid-phase Reynolds number  
 $Sc_G$  = gas-phase Schmidt number  
 $Sc_L$  = liquid-phase Schmidt number  
 $T$  = absolute temperature  
 $u_G$  = gas velocity in an interstice (velocity based on the empty tower cross section divided by the void fraction)  
 $u_L$  = liquid superficial velocity divided by the void fraction  
 $V$  = mass flow rate of vapor  
 $V_{\text{cell}}$  = volume of a void space, or “cell”, of the packing available for vapor and liquid flow  
 $We_L$  = liquid-phase Weber number

## Greek Symbols

$\alpha$  = universal scaling exponent for the divergence of the electrical conductivity near the percolation threshold; taken to have a value of 2 for linear resistors  
 $\delta$  = liquid film thickness  
 $\epsilon$  = bed void fraction

$\eta$  = scaling exponent for the two-phase pressure drop when  $(1 - C_L/C_L^*)$  is used to express distance from macroscopic flooding

$\lambda = \bar{m}G_{Gm}/G_{Lm}$

$\mu_G$  = gas-phase viscosity

$\mu_L$  = liquid-phase viscosity

$\nu$  = ratio of scaling exponents =  $\eta/\alpha$

$\rho_G$  = gas-phase mass density

$\rho_L$  = liquid-phase mass density

$\sigma_c$  = critical surface tension

$\sigma_L$  = liquid surface tension

$\sigma_W$  = surface tension of water

$\Psi$  = decay rate of the stretched exponential used in the calculation of  $\hat{\alpha}_m$

$\Omega$  = constant in the Wallis flooding equation

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