given by Coleman, Markovitz, and Noll (3). Oldroyd (4) obtained essentially the same results for $S^{<ij>}$ for the steady flow case by a different method.

For the particular flow studied by Johns,

$$v^r = 0 \quad v^\phi = \omega(r, \theta, t) \quad v^\theta = 0 \qquad (16)$$

$$h_1 = h_r = 1 \quad h_2 = h_\phi = r\sin\theta \quad h_3 = h_\theta = r \qquad (17)$$

Then

$$\nu = \frac{r \sin\theta}{\kappa} \frac{\partial\omega}{\partial r}(r, \theta, t); \quad \mu = \frac{\sin\theta}{\kappa} \frac{\partial\omega}{\partial\theta}(r, \theta, t) \qquad (18)$$

$$\kappa = r \sin\theta \sqrt{\left[\frac{\partial\omega(r, \theta, t)}{\partial r}\right]^2 + \left[\frac{\partial\omega(r, \theta, t)}{\partial\theta}\right]^2 \left(\frac{1}{r}\right)^2} \qquad (19)$$

$$\lambda(s) = \int_o^s \kappa dt \qquad (20)$$

Substituting Equations (18), (19), and (20) into Equation (14), we obtain Johns' equations for the extra stress tensor [his equations immediately preceding (15)]. Thus this flow pattern is curvilinear in the spherical coordinate system.

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The author wishes to thank Professor William R. Schowalter for many helpful suggestions in the writing of this paper.

NOTATION

$\mathbf{b}^{<i>}$ = orthonormal basis system
$\mathbf{e}^i$ = orthogonal basis system
$\mathbf{e}^{<i>}$ = orthonormal basis system
$F_{(t)}(\tau)$ = relative deformation gradient
f, g, q = separable functions of velocity gradient
g_{ij} = covariant components of the metric tensor
h_i = $\sqrt{g_{ii}}$ $i = 1, 2, 3$
$\mathbf{N}, \mathbf{N}_o$ = matrices defined in Equations (11) and (12)
$\underset{\sim}{\tilde{\mathbf{Q}}}(\tilde{\tau})$ = orthogonal matrix
r, θ, ϕ = spherical coordinates
$S^{<ij>}$ = physical components of $\mathbf{S}$
$\underset{\sim}{\mathbf{S}}$ = extra stress tensor
s = $t - \tau$ = time difference
t = time
v^i = contravariant components of velocity
x^i = orthogonal coordinates

Greek Letters

κ = function defined in Equation (8)
$\lambda(s)$ = function defined in Equation (9)
μ, ν = function defined in Equation (7)
ξ^i = mateiral coordinates
τ = past time
$\mathfrak{T}, \mathfrak{S}_1, \mathfrak{S}_2$ = viscometric functionals
$\tau(\kappa), \sigma_1(\kappa), \sigma_2(\kappa)$ = viscometric functions
ω = $v^2 = v^\phi$ = angular velocity

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Rectification in Continuous Contacting Equipment: On the Use of Correlations Obtained from Vaporization Experiments

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Continuous contacting equipment has frequently been employed in studies concerned with the mechanism of mass transfer in rectification. Experimental results have usually been interpreted on the assumption that the correlations for the vapor and liquid phase resistances to diffusional mass transfer in rectification are the same as, or at least similar in form to, those obtained from gas absorption or liquid vaporization experiments in the same equipment. For example, in much of the work with the popular wetted-wall column (*1* to *10*), the Chilton-Colburn (*15*) or Gilliland-Sherwood (*14*) correlations have been used as a basis in calculating the vapor film resistance.

Confining attention to rectification and liquid vaporization, a comparison of the two processes reveals several differences. Some of these, possible thermal effects (*11* to *13*) and the generally larger variation of physical properties in a rectification experiment (*7, 8, 10*), have been recognized. One effect which has not been taken into account by past experimentalists, however, is that due to the characteristic variation of the interfacial composition along the contacting equipment in rectification. In a vaporization experiment the interfacial composition may also change (due to a temperature drop resulting from evaporation of the liquid), but this change will normally be small compared to that encountered in the rectification of a mixture of high relative volatility, for example, one of the commonly used alcohol-water systems (*1* to *3*, *6, 7, 8, 16*).

In view of this differing behavior at the interface, the question arises: is it permissible to use correlations obtained from vaporization work in distillation studies, even if all other differences between the two processes can be assumed to be negligible, or somehow taken into account? What kind of discrepancy may one expect between the mass transfer coefficients for rectification and vaporization as a result of this composition effect, under experimental conditions relevant to past work?

In attempting an answer, attention was focused on vapor phase mass transfer in a wetted-wall column. By using theoretical solutions of the differential equations describing the steady state mass transfer process, the Stanton group for a system in which the interfacial composition is constant was compared to this group for certain systems of varying interfacial composition. Thus, the rectification of two binary systems of constant physical properties (vapor phase Schmidt number = 0.718), with the column oper-

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ating at total reflux, was considered. The relative volatility of one system was 10.0; that of the other was 2.0. (It may be noted that a mixture having a relative volatility of 10 is representative of the above-mentioned alcohol-water systems, at low concentrations of the more volatile component.) The liquid side resistance to mass transfer was assumed to be negligible. The Stanton number was calculated for column length to diameter ratios of 12 and 30 (other dimensions were also examined, but the conclusions were essentially unchanged), and Reynolds numbers of 2,000, 5,000 and 10,000. The Stanton number was also determined for a vaporization experiment with a system of the same physical properties, and under the same experimental conditions.

The mathematical technique employed was as follows. If a solution of the differential equations describing mass transfer is known for the particular case of a constant composition at the interface, then the solution for the case of a varying interfacial composition may be found using the principle of superposition (*17*). For the former case, the solution may be written in the form:

$$\frac{\overline{y}-\overline{y}_o}{y^*-\overline{y}_o} = F(z) = 1 - 8\sum_{n=0}^{\infty} A_n \exp\left[-B_n\xi\right] \qquad (1)$$

where $\xi = z/(N_{Re})(N_{Sc})d$, and A_n and B_n are constants tabulated in Table 1. For the case of laminar flow ($N_{Re} = 2{,}000$) they were taken from (*18*). For turbulent flow, use was made of values reported by Sleicher and Tribus (*19*) for heat transfer in a pipe. (Complete analogy was assumed between the processes of heat and mass transfer.) Three terms were found to satisfactorily represent the series in Equation (1) for the laminar flow case. For turbulent flow, the first two terms gave sufficient accuracy.

TABLE 1. CONSTANTS IN THE SERIES OF EQUATION (1) (FOR N_{Sc} = 0.718)

N_{Re}	A_1	A_2	A_3	B_1	B_2	B_3
2,000	0.1028	0.0122	0.0024	14.63	89.22	212.0
5,000	0.119	0.00208	—	84.0	1060.0	—
10,000	0.123	0.00200	—	140.0	1700.0	—

When the interfacial composition is a function of the distance, the principle of superposition gives the variation of the mean vapor mole fraction with distance to be:

$$\overline{y} = \overline{y}_o + [y^*(0) - \overline{y}_o]\,F(z) + \int_0^z \frac{dy^*(z)}{dz_1}\,F(z-z_1)\,dz_1 \qquad (2)$$

where $y^*(z)$ denotes that the interfacial composition now varies with distance along the column; $y^*(0)$ is the value of the interfacial mole fraction of the more volatile component at the point where the vapor enters the column, and z_1 is a dummy variable which, for a given value of z, takes on all values between zero and z. It is measured as shown in Figure 1.

From Equations (1) and (2) it is possible to calculate the variation of $\overline{y}$ with z in rectification and hence the average mass transfer coefficient, which is defined by the equation:

$$k = \frac{G}{Ha}\int_{\overline{y}_o}^{\overline{y}_T} \frac{d\overline{y}}{y^*(z) - \overline{y}} \qquad (3)$$

This definition leads to the familiar relationship (HTU) = G/ka between the mass transfer coefficient and the height of a transfer unit.

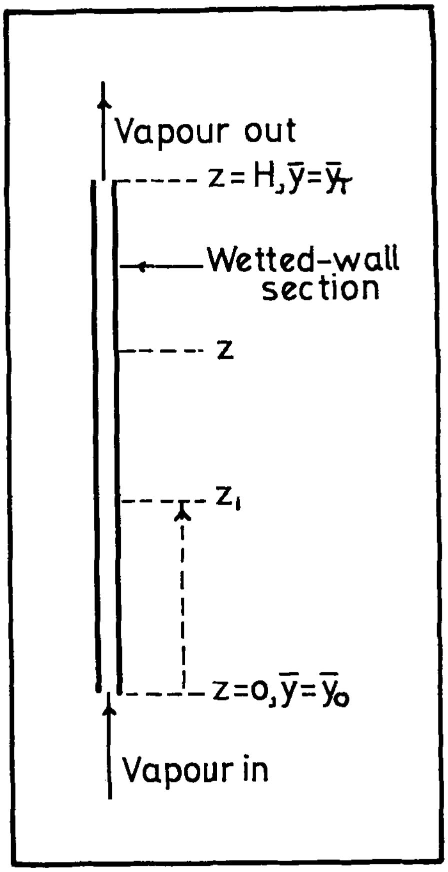

Fig. 1. Significance of some of the variables in Equations (2) and (3).

On the other hand, if the interfacial composition is constant, one obtains immediately from Equations (1) and (3) that:

$$k = -\frac{G}{Ha}\ln\left[1 - F(H)\right] \qquad (4)$$

and it can easily be shown that for this particular case the Stanton group is a function only of the Reynolds and Schmidt numbers, and the column length to diameter ratio. Therefore, in the present example, for each flow rate and column length, the Stanton number for the case of vaporization has a fixed value. It will be seen, however, that if y^* varies with distance, the Stanton group can be a strong function of the average composition in the column.

For the rectification case Equations (1) and (2) were solved by a numerical procedure, using an IBM 1620 computer. Calculation details are given elsewhere (*10*). The results are presented in Figure 2, where the ratio of the Stanton group for rectification, here designated $(N_{St})_R$, to that for vaporization, $(N_{St})_V$, is plotted against the average of the compositions at the top and bottom of the column.

From this figure, it is seen that, for the same physical properties and flow rates, the difference between the Stanton numbers for vaporization and rectification can be very pronounced. Because of the nature of the equilibrium relationship, the effect of a varying interfacial concentration is most strongly felt at low concentrations of the more volatile component. At higher concentrations, the equilibrium relationship flattens out, the interfacial concentration in distillation varies much less, and therefore $(N_{St})_R$ approaches $(N_{St})_V$ in magnitude. This is also true as the relative volatility of the mixture being rectified decreases.

The difference between $(N_{St})_R$ and $(N_{St})_V$ also depends on the flow rate. Figure 2 shows that for the laminar flow case $(N_{St})_R$ can be over two and a half times as great

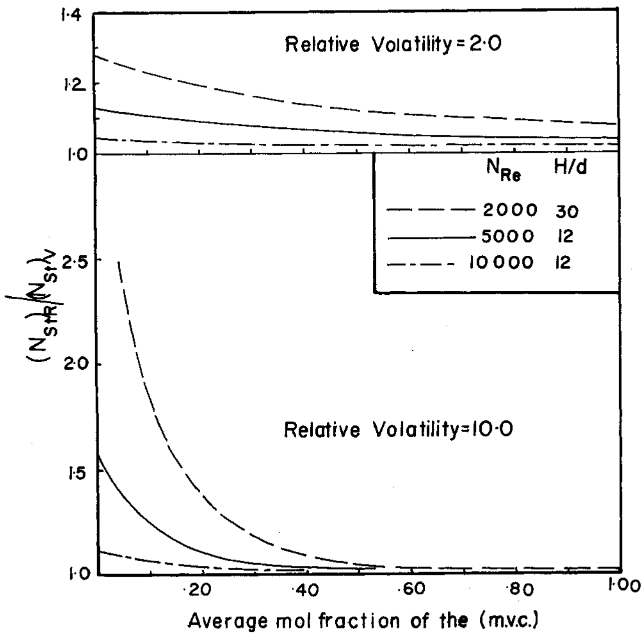

Fig. 2. Ratio of the Stanton numbers for rectification and vaporization.

as $(N_{St})_V$ and, for a Reynolds number of 5,000, approximately one and a half times as great. At a Reynolds number of 10,000, the two values differ but little.

An explanation for the significantly larger mass transfer coefficients (or Stanton numbers) predicted above for the case of rectification at the relatively low flow rates may be found elsewhere (*18*). Briefly, in a liquid vaporization experiment (where the interfacial composition is constant) as the diffusing vapor penetrates the gas stream, the rate of transfer decreases with distance along the column because the radial concentration gradients also decrease. In rectification, however, the interfacial composition varies with distance in such a way as to continuously reinforce the radial concentration gradients (that is the concentration of the more volatile component at the vapor-liquid interface continually increases in the direction of vapor flow). As a result, the mass transfer coefficients for the two processes differ in magnitude.

At the higher flow rate, where the mechanism of transfer is approximately one of diffusion across a thin vapor film near the interface, the differing behavior of the interfacial concentrations becomes unimportant, and the two mass transfer coefficients become roughly equal.

Although the present example has been confined to the case of mass transfer in a wetted-wall column, the problems raised should also apply (probably to a lesser extent) to other types of continuous contacting equipment, such as packed or disk (*16*) columns.

SUMMARY

Correlations for the vapor phase Stanton number obtained from vaporization experiments cannot in general be used in rectification investigations. It has been shown that, even in the absence of other complicating factors, the Stanton number for rectification may in certain cases differ significantly from that for vaporization, for the same Reynolds and Schmidt numbers and column dimensions. This difference results from the characteristic variation of the interfacial composition in rectification.

The present work should have particular bearing on investigations using the alcohol-water systems and other binaries of high relative volatility, especially at low flow rates. In several cases (*1*, *2*, *4*, *6* to *8*, *16*) correlations have been adopted from vaporization work under conditions where significant errors could result from such a procedure.

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NOTATION

a = interfacial area per unit height
c = total concentration
d = diameter of the column
D = diffusion coefficient
G = vapor flow rate (moles/time)
H = height of the column
(HTU) = height of a transfer unit
k = mass transfer coefficient
$(M.V.C.)$ = more volatile component
N_{Re} = Reynolds number, $(dU\rho/\mu)$
N_{Sc} = Schmidt number, $(u/\rho D)$
N_{St} = Stanton number, (k/cU)
U = average velocity (relative to the liquid interface)
$\bar{y}$ = mean vapor mole fraction
y^* = vapor mole fraction at the interface
y_o = vapor mole fraction at the column entrance
z = axial coordinate
z_1 = dummy variable in Equation (2)
μ = viscosity
ρ = density

Subscripts

o = value at bottom of column (that is, where vapor enters the contacting section)
R = the case of rectification
T = value at top of column
V = designates the case of vaporization

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