ACKNOWLEDGMENTS

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NOTATION

a = jet radius, cm
c = solute concentration disturbance, g-mole/cm^3
c^* = solute concentration in equilibrium with surroundings, g-mole/cm^3
$\mathcal{D}$ = solute diffusivity, cm^2/s
G_1-G_8 defined in Equation (13)
h = number of axes of symmetry about which the disturbance oscillates, dimensionless
i = $(-1)^{1/2}$
$I_h(\ )$ = modified Bessel function of the first kind, order h
k = disturbance wave number, cm^{-1}
K_c = proportionality constant, s^{-1}
$K_h(\ )$ = modified Bessel function of the second kind, order h
k_0 = mass transfer coefficient in the surroundings, cm/s
K_0 = k_0 times the solute distribution coefficient
L = jet length, cm
N_i = dimensionless groups defined in Table 1
p = pressure, dyne/cm^2
r = radial coordinate
R = gas constant
t = time, s
T = temperature, °K
u = velocity, cm/s
U = jet velocity, cm/s
z = axial coordinate

Greek Letters

β = growth constant, s^{-1}
$\bar{\beta}$ = dimensionless growth constant, $\beta\rho\, a^2/\mu$
Γ = solute adsorption, moles/cm^2
δ = adsorption equilibrium constant, cm
δ_m = mass transfer boundary layer thickness, cm
η = disturbance amplitude, cm
η_0 = initial disturbance amplitude, cm
θ = azimuthal coordinate
λ = disturbance wave length, cm
μ = viscosity, g/cm s
ν = kinematic viscosity, cm^2/s
ξ = dimensionless wave number
ξ_1, ξ_2 defined in Equation (13)
ρ = density, g/cm^3
σ = surface tension, g/s^2

Subscripts

a, s = at jet surface
i = initial
0 = undisturbed
r, z, θ = coordinates
$\wedge$ = surroundings
$*$ = most unstable

LITERATURE CITED

Alterman, Z., "Capillary Instability of a Liquid Jet," *Phys. Fluids*, **4**, 955 (1961).

Anshus, B. E., "The Effect of Surfactants on the Breakup of Cylinders and Jets," *J. Colloid Interface Sci.*, **43**, 113 (1973).

Berg, J. C., and A. Acrivos, "The Effect of Surface Active Agents on Convection Cells Induced by Surface Tension," *Chem. Eng. Sci.*, **20**, 737 (1965).

Burkholder, H. C., "The Effects of Surface Adsorption, Heat Transfer and Mass Transfer on the Stability of Capillary Jets," Ph.D. dissertation, Univ. Washington, Seattle (1973).

———., and J. C. Berg, "The Effect of Mass Transfer on Laminar Jet Breakup, II. Liquid Jets in Liquids," *AIChE J.*, **20**, 000 (1974).

Haenlein, A., *Forschung*, **2**, 139 (1932).

Handbook of Chemistry and Physics, CRC Publ. Co., Cleveland, Ohio (1962).

Kayser, W. V., and J. C. Berg, "Spontaneous Convection in the Vicinity of Liquid Meniscuses," *Ind. Eng. Chem. Fundamentals*, **10**, 526 (1971).

Levich, V. G., *Physicochemical Hydrodynamics*, Prentice Hall, Englewood Cliffs, N. J. (1962).

Linde, H., S. Pfaff, and Chr. Zirkel, "Strömungsuntersuchungen zur hydrodynamischen Instabilität flüssig-gasförmiger Phasengrenzen mit Hilfe der Kapillarspaltmethode," *Z. Phys. Chem.*, **225**, 72 (1964).

Ling, C.-H., and W. C. Reynolds, "Non-parallel flow corrections for the stability of shear flows," *J. Fluid Mech.*, **59**, 571 (1973).

Palmer, H. J., and J. C. Berg, "Hydrodynamic stability of surfactant solutions heated from below," *ibid.*, **51**, 385 (1972).

Pearson, J. R. A., "On convection cells induced by surface tension," *ibid.*, **4**, 489 (1958).

Plateau, M. T., *Statique Expérimentale et Théorique des Liquides soumis aux seules Forces Moléculaires*, Paris (1873).

Prandtl, L., *Fluid Dynamics*, Hafner, New York (1952).

Rayleigh, Lord, "On the Instability of Jets," *Proc. London Math. Soc.*, **10**, 4 (1878).

———., "On Capillary Phenomena of Jets," *Proc. Royal Soc. (London)*, **29**, 71 (1879).

———., "On the Instability of a Cylinder of Viscous Liquid under Capillary Force," *Phil. Mag.*, **34**, 145 (1892).

Savart, F., "Mémoire sur la Constitution des Veines Liquides Lancées par des Orifices Circulaires en mince paroi," *Ann. Chim. Phys.*, **53**, 337 (1833).

Sawistowski, H., "Interfacial Phenomena," in *Recent Advances in Liquid-Liquid Extraction*, C. Hanson, (ed.) Pergamon Press, Oxford (1971).

Sternling, C. V., and L. E. Scriven, "Interfacial Turbulence: Hydrodynamic Instability and the Marangoni Effect," *AIChE J.*, **5**, 514 (1959).

Sterling, A. M., "The Instability of Capillary Jets," Ph.D. dissertation, Univ. Washington, Seattle (1969).

Weber, C., "On the Breakup of a Fluid Jet," *Z. Angew. Math. Mech.*, **11**, 136 (1931).

Part II. Liquid Jets in Liquids

The instability and breakup of laminar liquid jets in liquid surroundings is investigated for situations where solute transfer across the jet interface renders the system susceptible to Marangoni convection. This work parallels Part I (Burkholder and Berg, 1974) on the effect of mass transfer on the breakup of laminar liquid jets in gases. Behavior in liquid-liquid systems, however, differs significantly from that for liquid-gas systems and cannot be inferred from the analysis of the latter. Linear hydrodynamic

stability analysis reveals that transfer either into or out of the jet may be either stabilizing (longer jets) or destabilizing depending on system physical properties and mass transfer rate. Solute adsorption may strongly counteract the effects of the mass transfer but has only a small effect on jet stability in the absence of mass transfer. The predicted mass transfer effects conform qualitatively to the experimental results of Meister and Scheele (1969) for acetone transfer between benzene jets and water.

SCOPE

The breakup of laminar liquid jets in liquids was first investigated by Tomotika (1935), who applied Rayleigh's linear hydrodynamic stability theory (Rayleigh 1878, 1879, 1892) to a zero density viscous jet in zero density viscous surroundings. Meister and Scheele (1967, 1969) generalized Tomotika's model to liquids with nonzero density and showed that jet lengths predicted by their theory were in agreement with experiments for pure liquids without interphase mass transfer. Because the breakup of liquid jets in liquids is important in the design and operation of spray extraction columns, where the breakup is accompanied by mass transfer, Meister and Scheele (1969) also measured jet lengths for the case in which there was transfer of acetone between benzene jets and water. Mass transfer into the jet was found to produce significantly longer jets than transfer out, but no explanation or analysis of this effect was provided.

As in our earlier study of liquid jets in gases, Part I, hereafter referred to as (I), the influence of mass transfer on jet breakup derives from the potential in such cases for the development of longitudinal variations in composition and hence interfacial tension along the jet prior to breakup. This may generate convection in either or both phases which in turn can either inhibit or reinforce the growth of the surface corrugations that ultimately lead to jet breakup. This study predicts theoretically the effect of solute transfer between a dilute binary liquid jet and dilute binary liquid surroundings using linear stability analysis and compares qualitatively the theoretical predictions with the experimental data of Meister and Scheele.

CONCLUSIONS AND SIGNIFICANCE

The most important theoretical predictions are: (1) mass transfer of a surface tension lowering solute either into or out of the jet may be either stabilizing (longer jets) or destabilizing (shorter jets) depending on system physical properties and mass transfer rate; (2) surface adsorption may strongly counteract either the stabilizing or destabilizing effects of the mass transfer on the jet; (3) surface adsorption, including that of strong surface active agents, has only a very small effect on jet stability in the absence of mass transfer; and (4) the wavelength of the most unstable disturbance, hence the ultimate drop size may either increase or decrease for transfer either into or out of the jet. The predicted mass transfer effects conform qualitatively to the experimental results of Meister and Scheele.

The phenomena studied here may have important implications in deciding which phase to disperse in spray liquid-liquid extraction columns. Unfortunately, the mass transfer phenomena are so complicated that it will often not be possible to predict whether mass transfer will be stabilizing or destabilizing in a given situation without numerical solution of the characteristic equation presented herein.

The application of linear hydrodynamic stability analysis to the breakup of jets was, as described elsewhere (Burkholder, 1973), developed by Lord Rayleigh (1878, 1879, 1892). Tomotika (1935) applied Rayleigh's theory to a model consisting of a zero density viscous jet in zero density viscous surroundings and obtained results in good agreement with Taylor's previous experimental data for the breakup of very viscous liquid threads in very viscous liquids (Taylor, 1934). Meister and Scheele (1967, 1969) generalized Tomotika's model to liquids with nonzero density and showed that predicted jet lengths from their theory were in agreement with their experiments for pure liquids, that is, in the absence of interphase mass transfer. Meister and Scheele (1969) also measured the jet lengths for the case in which there was transfer of acetone between benzene jets and water. They found that transfer in both directions was stabilizing relative to the no mass transfer case and that transfer into the jet produced longer jets than transfer out. While they suggested that the former effect resulted from the reduction in mean interfacial tension level caused by the presence of a tension lowering solute (acetone), they did not offer an explanation for the effect of mass transfer direction. Sawistowski (1973), although making no reference to Meister and Scheele, suggested that the latter type of phenomenon results from quasi-equilibration between the jet and surroundings which (for transfer into the jet) causes the solute concentration to be greater at the thin neck or valley of the growing interface corrugation than at the bulge or peak. Thus, the interfacial tension is lower (for a tension lowering solute) at the valley than at the peak. The interface then expands toward the peak and causes liquid transport from the valley to the peak, thus reinforcing jet breakup. Thus, Sawistowski's explanation suggests that transfer into the jet is destabilizing while Meister and Scheele's results show that transfer into the jet is stabilizing. A possible explanation for the results of Meister and Scheele is suggested by the results of (I) which imply that either stabilization or destabilization may occur without quasi-equilibration of the phases. Whether the mass transfer is stabilizing or destabilizing depends upon which phase has the stronger Marangoni convection as dictated by the physical properties of the system. The present situation is thus similar to the well known Sternling-Scriven problem (Sternling and Scriven, 1959). The objectives of the present study are thus to: (1) perform a linear hydrodynamic stability analysis on the system to predict theoretically the effect of solute transfer between a dilute binary liquid jet and dilute binary liquid surroundings and (2) compare qualitatively the theoretical predictions with the experimental results of Meister and Scheele.

THEORETICAL DEVELOPMENT

The model to be analyzed is an infinite cylindrical column of a nonvolatile, incompressible, Newtonian liquid in steady laminar plug flow through a second nonvolatile incompressible Newtonian liquid. The flow is assumed to be so slow that aerodynamic effects are negligible.* A solute is present in small amounts in both phases, and the surface is assumed to be in local adsorption equilibrium with both bulk phases. The bulk phases are thus also in local equilibrium at the interface. In the undisturbed state the solute concentration is assumed to vary linearly with radial position in both the jet and the surroundings. The densities, viscosities, and solute diffusivities are constant in both phases, and the interfacial tension is linearly proportional to the solute concentration at the interface.

A small arbitrary disturbance, in accordance with Rayleigh's postulates, is imposed upon the system, causing a deflection of the jet surface and perturbations in the radial and axial velocity components, the pressure, and the solute concentration in both phases. As a consequence of these changes, the interfacial tension may vary axially along the jet. The variation of all quantities in the azimuthal (θ) direction is neglected with the exception of the interface deflection.

The disturbance must satisfy the linearized Navier-Stokes and diffusion equations in both phases, which are

$$\nabla \cdot \underline{u} = 0 \tag{1}$$

$$\nabla \cdot \hat{\underline{u}} = 0 \tag{2}$$

$$\frac{\partial \underline{u}}{\partial t} = -\frac{1}{\rho}\nabla p + \nu\nabla^2 \underline{u} \tag{3}$$

$$\frac{\partial \hat{\underline{u}}}{\partial t} = -\frac{1}{\hat{\rho}}\nabla \hat{p} + \hat{\nu}\nabla^2 \hat{\underline{u}} \tag{4}$$

$$\frac{\partial c}{\partial t} + u_r\frac{\partial c_0}{\partial r} = D\nabla^2 c \tag{5}$$

$$\frac{\partial \hat{c}}{\partial t} + \hat{u}_r\frac{\partial \hat{c}_0}{\partial r} = \hat{D}\nabla^2 \hat{c} \tag{6}$$

where r is the radial coordinate measured from the jet axis, and u_r is the radial velocity perturbation.

The equations are solved subject to the linearized boundary conditions which express continuity of velocity, shear stress, normal stress and solute molar flux, and phase equilibrium at the jet surface $r = a$. These are

$$u_r = \hat{u}_r \quad \text{continuity of radial velocity} \tag{7}$$

$$u_z = \hat{u}_z \quad \text{continuity of axial velocity} \tag{8}$$

$$\mu\left(\frac{\partial u_z}{\partial r} + \frac{\partial u_r}{\partial z}\right) - \hat{\mu}\left(\frac{\partial \hat{u}_z}{\partial r} + \frac{\partial \hat{u}_r}{\partial z}\right) - \frac{\partial \sigma}{\partial c}\frac{\partial c}{\partial z} = 0$$

$$\text{continuity of shear stress} \tag{9}$$

$$\hat{p} - 2\hat{\mu}\frac{\partial \hat{u}_r}{\partial r} - p + 2\mu\frac{\partial u_r}{\partial r} - \frac{\sigma_0}{a^2}(1 - h^2 - k^2a^2)\eta$$

$$+ \frac{\partial \sigma}{\partial c}\frac{c}{a} = 0 \quad \text{continuity of normal stress} \tag{10}$$

$$\delta\left[\frac{\partial c}{\partial t} + c_0\left(\frac{u_r}{r} + \frac{\partial u_z}{\partial z}\right)\right] + D\frac{\partial c}{\partial r} - \hat{D}\frac{\partial \hat{c}}{\partial r} = 0$$

$$\text{continuity of solute molar flux} \tag{11}$$

$$\hat{c} = mc \quad \text{phase equilibrium} \tag{12}$$

where η is the displacement of the jet surface from its mean position and is related to the radial velocity by the equation $[u_r = \partial\eta/\partial t]_{r=a}$; δ is the adsorption equilibrium constant with respect to the jet phase and is defined by the equation $\Gamma = \delta\, c_s$ where c_s is the solute concentration in the jet sublayer; σ and $\partial\sigma/\partial c$ are the interfacial tension and concentration coefficient of interfacial tension; and the subscripts r and z refer to the radial and axial components.

It is to be noted that, as in (I), interfacial viscosity and diffusivity have not been incorporated into this model.

Simultaneous solution of the equations and boundary conditions and nondimensionalization of the results yields the following characteristic equation relating β, the dimensionless growth constant of the disturbance to ξ, the dimensionless wave number for any given set of values for the ten dimensionless groups, summarized in Table 1, which describes the properties of the system:

$$\bar{\beta}^2 \Bigl\{ \xi\frac{I_0(\xi)}{I_1(\xi)}\Bigl[<(\xi_1^2 + \xi^2) - 2\,N_{VS}\xi^2> \hat{\xi}_1\frac{K_0(\hat{\xi}_1)}{K_1(\hat{\xi}_1)}$$

$$+ N_{VS}(\hat{\xi}_1^2 - \xi^2)\,\xi_1\frac{I_0(\xi_1)}{I_1(\xi_1)} + <N_{VS}(\hat{\xi}_1^2 + \xi^2)$$

$$- (\xi_1^2 + \xi^2)> \xi\frac{K_0(\xi)}{K_1(\xi)} + H_1 \Bigr]$$

$$+ N_{DN}\xi\frac{K_0(\xi)}{K_1(\xi)}\Bigl[(\xi_1^2 - \xi^2)\,\hat{\xi}_1\frac{K_0(\hat{\xi}_1)}{K_1(\hat{\xi}_1)}$$

$$+ <N_{VS}(\hat{\xi}_1^2 + \xi^2) - 2\xi^2> \xi_1\frac{I_0(\xi_1)}{I_1(\xi_1)}$$

$$+ <(\xi_1^2 + \xi^2) - N_{VS}(\hat{\xi}_1^2 + \xi^2)> \xi\frac{I_0(\xi)}{I_1(\xi)} + H_2 \Bigr] \Bigr\}$$

$$+ \bar{\beta}\Bigl\{ 2(1 - N_{VS})\xi^2 \Bigl[<(\xi_1^2 + \xi^2) - 2\,N_{VS}\xi^2>$$

$$\xi\frac{I_0(\xi)}{I_1(\xi)}\hat{\xi}_1\frac{K_0(\hat{\xi}_1)}{K_1(\hat{\xi}_1)} + <N_{VS}(\hat{\xi}_1^2 + \xi^2) - (\xi_1^2 + \xi^2)>$$

$$\xi\frac{I_0(\xi)}{I_1(\xi)}\xi\frac{K_0(\xi)}{K_1(\xi)} + <2\xi^2(N_{VS} - 1)>$$

$$\xi_1\frac{I_0(\xi_1)}{I_1(\xi_1)}\hat{\xi}_1\frac{K_0(\hat{\xi}_1)}{K_1(\hat{\xi}_1)} + <2\xi^2 - N_{VS}(\hat{\xi}_1^2 + \xi^2)> \xi\frac{K_0(\xi)}{K_1(\xi)}$$

(continued on next page)

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* Fenn and Middleman (1969) have determined that such will be the case if the Weber number, $N_{WE} = \hat{\rho}aU^2/\sigma$, is less than 5.3.

$$\xi_1 \frac{I_0(\xi_1)}{I_1(\xi_1)} + (\xi_1{}^2 - \xi^2) \left\langle \xi \frac{K_0(\xi)}{K_1(\xi)} - \hat{\xi}_1 \frac{K_0(\hat{\xi}_1)}{K_1(\hat{\xi}_1)} \right\rangle$$

$$+ N_{VS} (\hat{\xi}_1{}^2 - \xi^2) \left\langle \xi \frac{I_0(\xi)}{I_1(\xi)} - \xi_1 \frac{I_0(\xi_1)}{I_1(\xi_1)} \right\rangle + H_3 \Big] \Big\}$$

$$- N_{SU}(1 - h^2 - \xi^2)\xi^2 \Big[(\xi_1{}^2 - \xi^2)$$

$$\left\langle \hat{\xi}_1 \frac{K_0(\hat{\xi}_1)}{K_1(\hat{\xi}_1)} - \xi \frac{K_0(\xi)}{K_1(\xi)} \right\rangle + N_{VS}(\hat{\xi}_1{}^2 - \xi^2)$$

$$\left\langle \xi_1 \frac{I_0(\xi_1)}{I_1(\xi_1)} - \xi \frac{I_0(\xi)}{I_1(\xi)} \right\rangle + H_4 \Big] = 0 \quad (13)$$

[Equation (13) describes axisymmetric disturbances for $h = 0$ and asymmetric disturbances for $h = 1$]
where

$$H_1 = N_{MA} H_5 \left[H_6 - \frac{H_7}{H_{13}} \right] (H_{10} - H_{11})$$

$$+ \hat{N}_{MA} H_5 \left[H_8 \left(H_{11} + H_{12} - \frac{H_{11}}{H_{13}} - 1 \right) \right.$$

$$\left. - H_9 \left(H_{10} + H_{12} - \frac{H_{10}}{H_{13}} - 1 \right) \right]$$

$$+ N_{EL} H_5 \left(H_{12} + \frac{1}{H_{13}} - 2 \right) (H_{10} - H_{11})$$

$$H_2 = N_{MA} H_5 \left[H_6 \left(H_{10} + H_{13} + \frac{H_{13}}{H_{11}} + 1 \right) \right.$$

$$\left. - H_7 \left(H_{10} + H_{12} + \frac{H_{12}}{H_{11}} + 1 \right) \right]$$

$$+ \hat{N}_{MA} H_5 \left(H_8 + \frac{H_9}{H_{11}} \right) (H_{12} - H_{13})$$

$$+ N_{EL} H_5 (H_{10} + 1)(H_{12} - H_{13})$$

$$H_3 = N_{MA} H_5 (H_6 H_{13} - H_7 H_{12})(H_{10} - H_{11})$$

$$+ \hat{N}_{MA} H_5 (H_8 H_{11} - H_9 H_{10})(H_{13} - H_{12})$$

$$+ N_{EL} H_5 (H_{11} - H_{10})(H_{13} - H_{12})$$

$$H_4 = N_{MA} H_5 (H_6 - H_7)(H_{10} - H_{11})$$

$$+ \hat{N}_{MA} H_5 (H_8 - H_9)(H_{12} - H_{13})$$

$$+ N_{EL} H_5 (H_{10} - H_{11})(H_{12} - H_{13})$$

$$H_5 = \frac{\xi^2 \dfrac{K_0(\hat{\xi}_2)}{\hat{\xi}_2 K_1(\hat{\xi}_2)} \quad \dfrac{I_0(\xi_2)}{\xi_2 I_1(\xi_2)}}{\dfrac{K_0(\hat{\xi}_2)}{\hat{\xi}_2 K_1(\hat{\xi}_2)} + N_{DI} \dfrac{I_0(\xi_2)}{\xi_2 I_1(\xi_2)} + \bar{\beta} N_{SS} \dfrac{K_0(\hat{\xi}_2)}{\hat{\xi}_2 K_1(\hat{\xi}_2)} \quad \dfrac{I_0(\xi_2)}{\xi_2 I_1(\xi_2)}}$$

$$H_6 = \frac{\int^a s I_0(ms) I_1(ls)\, ds}{a^2 I_0(\xi_2)\ I_1(\xi_1)}$$

$$H_7 = \frac{\int^a s I_0(ms) I_1(ks)\, ds}{a^2 I_0(\xi_2) I_1(\xi)}$$

$$H_8 = \frac{\int^a s K_0(\hat{m}s) K_1(\hat{l}s)\, ds}{a^2 K_0(\hat{\xi}_2) K_1(\hat{\xi}_1)}$$

TABLE 1. DIMENSIONLESS GROUPS IN EQUATION (13)

$N_{SU} = \dfrac{\sigma_0 \rho a}{\mu^2}$	Suratman number
$N_{MA} = \dfrac{\left(\dfrac{\partial \sigma}{\partial c}\right)\left(\dfrac{\partial c_0}{\partial r}\right)_a a^2}{\mu D}$	Marangoni number in the jet
$\hat{N}_{MA} = \dfrac{\left(\dfrac{\partial \sigma}{\partial c}\right)\left(\dfrac{\partial \hat{c}_0}{\partial r}\right)_a a^2}{\mu D}$	Marangoni number in the surroundings
$N_{EL} = \dfrac{\left(\dfrac{\partial \sigma}{\partial c}\right)^2 (c_0)_a}{R\, T\, \mu\, D}$	Surface elasticity number
$N_{DI} = \dfrac{m\hat{D}}{D}$	Distribution number
$N_{SC} = \dfrac{\mu}{\rho D}$	Schmidt number
$N_{SS} = \dfrac{-\left(\dfrac{\partial \sigma}{\partial c}\right)\mu}{a\, R\, T\, p\, D}$	Interface Schmidt number
$N_{DN} = \dfrac{\hat{\rho}}{\rho}$	Density ratio
$N_{VS} = \dfrac{\hat{\mu}}{\mu}$	Viscosity ratio
$N_{DF} = \dfrac{D}{\hat{D}}$	Diffusivity ratio

$$H_9 = \frac{\int^a s K_0(\hat{m}s) K_1(ks)\, ds}{a^2 K_0(\hat{\xi}_2) K_1(\xi)}$$

$$H_{10} = \hat{\xi}_1 \frac{K_0(\hat{\xi}_1)}{K_1(\hat{\xi}_1)}$$

$$H_{11} = \xi \frac{K_0(\xi)}{K_1(\xi)}$$

$$H_{12} = \xi_1 \frac{I_0(\xi_1)}{I_1(\xi_1)}$$

$$H_{13} = \xi \frac{I_0(\xi)}{I_1(\xi)}$$

$\bar{\beta} = \dfrac{\beta \rho a^2}{\mu}$	dimensionless growth constant
$\xi = ka$	dimensionless wavenumber
$\xi_1 = (\xi^2 + \bar{\beta})^{1/2}$	dimensionless wavenumber for momentum transfer in the jet
$\hat{\xi}_1 = (\xi^2 + \bar{\beta} N_{DN}/N_{VS})^{1/2}$	dimensionless wavenumber for momentum transfer in the surroundings
$\xi_2 = (\xi^2 + \bar{\beta} N_{SC})^{1/2}$	dimensionless wavenumber for mass transfer in the jet

$\hat{\xi}_2 = (\xi^2 + \bar{\beta} N_{SC} N_{DF})^{1/2}$ dimensionless wavenumber for mass transfer in the surroundings

Equation (13) contains the results of all previous theoretical analyses of the stability of liquid jets in liquids. For example, setting N_{MA}, $\hat{N}_{MA}$, N_{EL}, N_{DI}, and $N_{SS} = 0$, dividing through by N_{VS}, converting the dimensionless growth constant to a dimensional one and rearranging reduces Equation (13) to Equation (C-72) in Meister (1966). Equation (13) in this paper and Equation (13) in (I) can be collapsed together after much algebraic manipulation as shown by Burkholder (1973).

After rearrangement Equation (13) is solved numerically for a number of arbitrary sets of values for the dimensionless groups by the same methods discussed in (I). Only one situation was encountered for axisymmetric disturbances where the principle of exchange of stabilities did not hold, and this situation was near the upper limit of experimentally attainable values for the Marangoni number. Hence, oscillatory instability is not expected in experimental situations.

THEORETICAL RESULTS AND DISCUSSION

Figure 1 shows the effect of adsorption (as characterized by the surface elasticity number N_{EL}) on the dimensionless growth constant of the most unstable axisymmetric disturbance ($\bar{\beta}^*$) as a function of N_{SU} with the remaining dimensionless groups held constant. Increasing values of the growth constant correspond to predicted decreases in jet length. Adsorption is seen to be only very weakly destabilizing in the absence of mass transfer (regardless of the value of N_{SU}) even for large surfactant surface concentrations. Thus even the presence of a spread surfactant monolayer on the jet surface has virtually no effect on the stability of liquid jets in liquids in the absence of mass transfer.

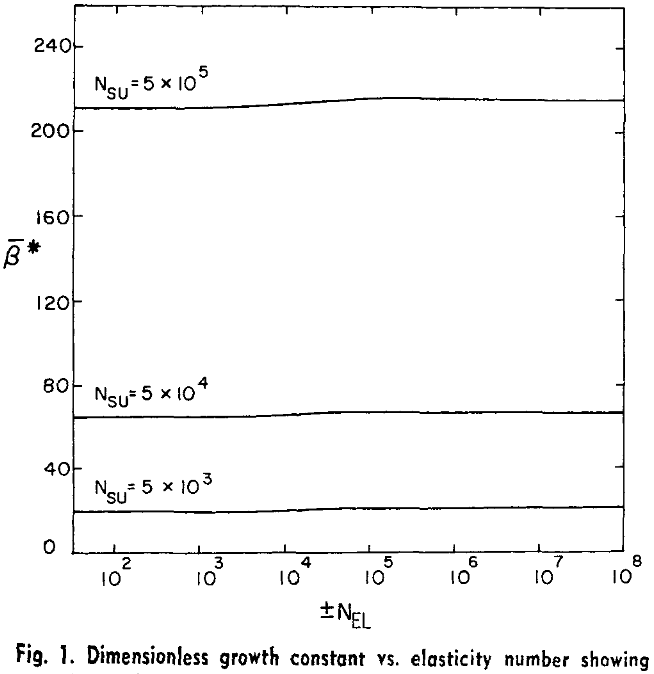

Fig. 1. Dimensionless growth constant vs. elasticity number showing the effect of solute adsorption or the presence of surfactants on jet stability in the absence of mass transfer. Other dimensionless groups have values: $N_{MA} = 0$, $\hat{N}_{MA} = 0$, $N_{SS} = 0.04$, $N_{DN} = 1$, $N_{VS} = 1$, $N_{DF} = 1$, $N_{DI} = 1$, $N_{SC} = 10^3$.

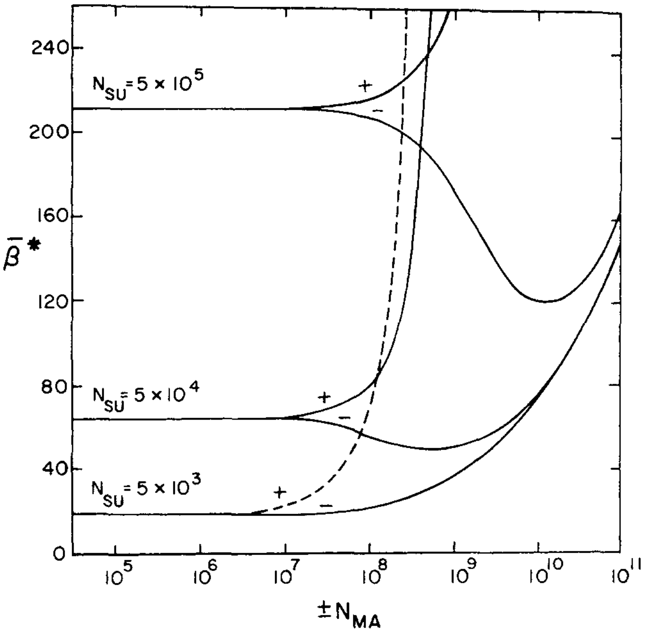

Fig. 2. Dimensionless growth constant vs. Marangoni number. + and − denote the sign of $N_{MA} = \hat{N}_{MA}$ corresponding to each branch of the curves for various values of N_{SU}. Other groups are set at: $N_{EL} = 0$, $N_{SS} = 0.04$, $N_{DN} = 1$, $N_{VS} = 1$, $N_{DF} = 1$, $N_{DI} = 1$, $N_{SC} = 10^3$. Dashed line for $N_{SU} = 5 \times 10^3$ indicates that there is some uncertainty concerning the exact location of the curve due to convergence difficulties in the solution of Equation (13) for *this case*.

Figure 2 shows the effect of mass transfer, characterized by N_{MA} or $\hat{N}_{MA}$, on jet stability as a function of the interfacial tension level, characterized by N_{SU}. The effect is seen to become significant at Marangoni numbers of approximately ± 10^7, values well within the range of those that might be encountered in practice. Transfer of a tension lowering solute out of the jet (positive N_{MA}) is seen to be destabilizing. Transfer in the reverse direction, however, in sharp contrast to the behavior of liquid jets in gases, is stabilizing only for smaller rates of mass transfer and becomes destabilizing as the rate increases. Thus *mass transfer in either direction* shortens the jet if the transfer rate is great enough. The maximum stabilization that can occur at intermediate rates increases with increasing N_{SU} (increasing interfacial tension), but very small growth constants are never predicted. Finally, for very large transfer rates into the jet, the growth constant becomes independent *of* N_{SU}.

Figures 3 and 4 show the effect of the density and viscosity ratios (N_{DN} and N_{VS}) on a system with $N_{SU} = 5 \times 10^4$ (the middle curve in Figure 2). Increasing either N_{DN} or N_{VS} from a value of 1 to a value of 10 does not change the sense of the mass transfer effect, but decreasing either from a value of 1 to a value of 0.1 reverses the sense of the mass transfer effect (transfer out is stabilizing, transfer in destabilizing). Numerical calculations for this case show that if either N_{DN} or N_{VS} is $> 0.85 \pm .025$ transfer of a tension lowering solute out of the jet is destabilizing and into the jet is stabilizing (at low transfer rates); if either N_{DN} or N_{VS} is $< 0.85 \pm .025$, transfer out is stabilizing and transfer in is destabilizing. It should be noted that as the values for either N_{DN} or N_{VS} move away from 1 in either direction the onset of the Marangoni effect occurs at smaller Marangoni numbers (smaller mass transfer rates).

Figure 5 shows the effect of the solute diffusivity in the surroundings on jet stability. Since continuity of solute molar flux must always be maintained at the jet surface, an increase in the diffusivity of the surroundings must be accompanied by a corresponding decrease in the solute concentration gradient in the surroundings, and conversely. As shown, decreasing the solute diffusivity in the surroundings ($N_{DF} > 1$) strengthens the mass transfer effect regardless of whether it is stabilizing or destabilizing. Likewise, increasing the solute diffusivity in the surroundings ($N_{DF} < 1$) weakens the mass transfer effect.

The results in Figures 2 to 5 may be explained on qualitative physical grounds with reference to Figure 6. Figure 6a shows an undisturbed section of the jet and surroundings with lines of constant solute concentration sketched in. The axisymmetric interface deformation of the jet then creates new interface at the peaks of the corrugations and reduces the area at their valleys causing the shift in the lines of constant concentration shown in Figure 6b. Thus, liquid from both bulk phases reaches the interface at the peak and leaves the interface at the valley. For transfer out of the jet the liquid reaching the interface at the peak from the jet phase is richer (but from the surrounding phase is leaner) in the solute than the original undisturbed interface. If the physical properties of the two phases are such that the effective convection to the interface from the jet is greater than that from the surroundings, it becomes richer in the solute at the peak and leaner at the valley. For a tension lowering solute (the usual situation) the tension becomes lower at the peak than at the valley. The resulting interfacial tension gradient generates interfacial flow away from the peaks, as shown in Figure 6c, and thus tends to oppose the necking down process which ultimately leads to jet breakup. Similar reasoning shows that transfer into the jet has a destabilizing effect when the effective convection is greater in the jet. Both effects would be reversed for tension raising solutes or for situations where the effective convection is greater in the surroundings.

Figure 7 shows the effect of surface adsorption, as char-

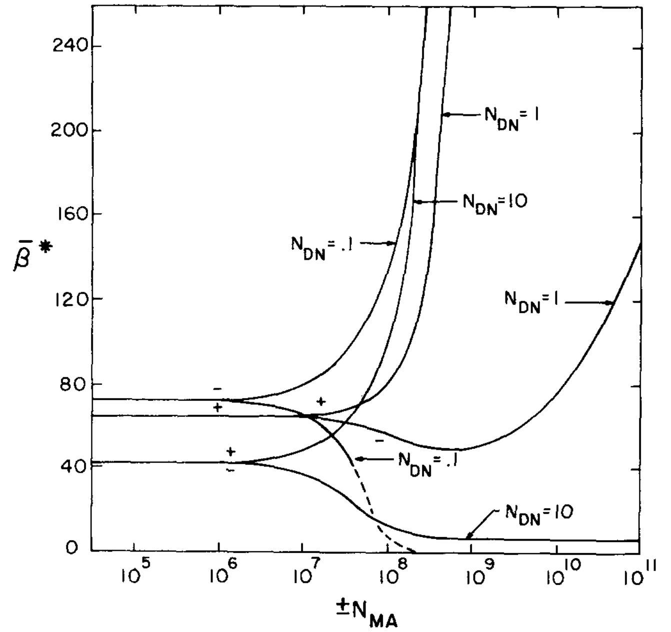

Fig. 3. Dimensionless growth constant vs. Marangoni number (+ and − denote sign of N_{MA}, $\hat{N}_{MA}$) showing the effect of mass transfer on jet stability as a function of N_{DN}. Other dimensionless groups are set at: $N_{SU} = 5 \times 10^4$, $N_{EL} = 0$, $N_{SS} = 0.04$, $N_{VS} = 1$, $N_{DF} = 1$, $N_{DI} = 1$, $N_{SC} = 10^3$. Dashed line indicates uncertainty in curve location due to convergence difficulties in solving Equation (13).

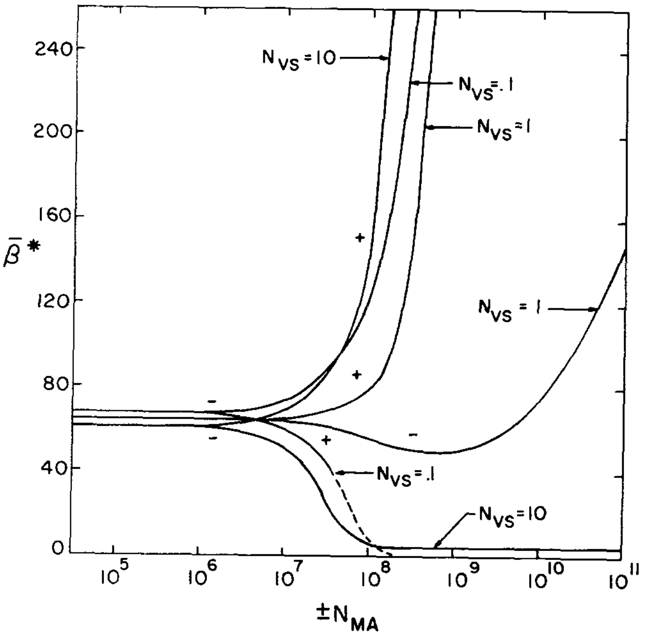

Fig. 4. Dimensionless growth constant vs. Marangoni number (+ and − denote sign of N_{MA}, $\hat{N}_{MA}$) showing the effect of mass transfer on jet stability as a function of N_{VS}. Other dimensionless groups are set at: $N_{SU} = 5 \times 10^4$, $N_{EL} = 0$, $N_{SS} = 0.04$, $N_{DN} = 1$, $N_{DF} = 1$, $N_{DI} = 1$, $N_{SC} = 10^3$. Dashed line indicates uncertainty in curve location due to convergence difficulties in solving Equation (13).

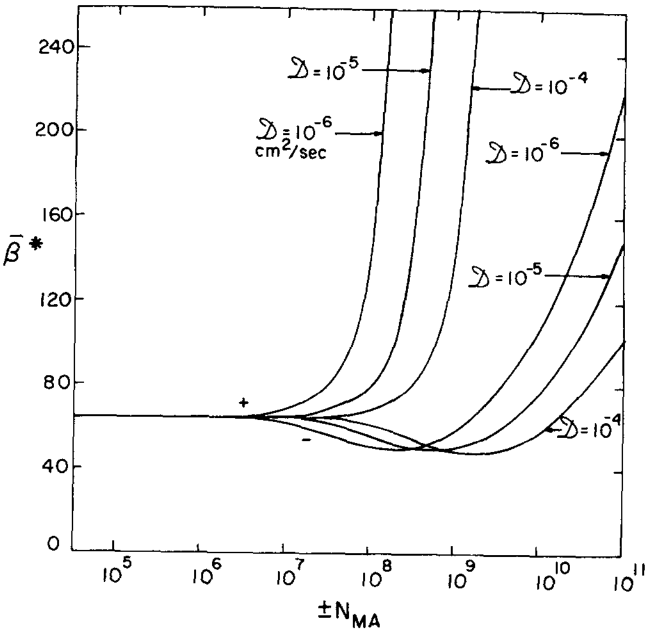

Fig. 5. Dimensionless growth constant vs. Marangoni number (+ and − denote sign of N_{MA}) showing the effect of mass transfer on jet stability as a function of diffusivity in the surroundings, $\hat{D}$. Diffusivity inside the jet is set at $D = 10^{-5}$ cm²/s, and $\hat{D}$ and $(\partial \hat{c}_0/\partial r)_a$ are varied simultaneously such that continuity of molar flux is maintained at the jet surface. Other dimensionless groups are set at $N_{SU} = 5 \times 10^4$, $N_{EL} = 0$, $N_{SS} = 0.04$, $N_{DN} = 1$, $N_{VS} = 1$, $N_{SC} = 10^3$.

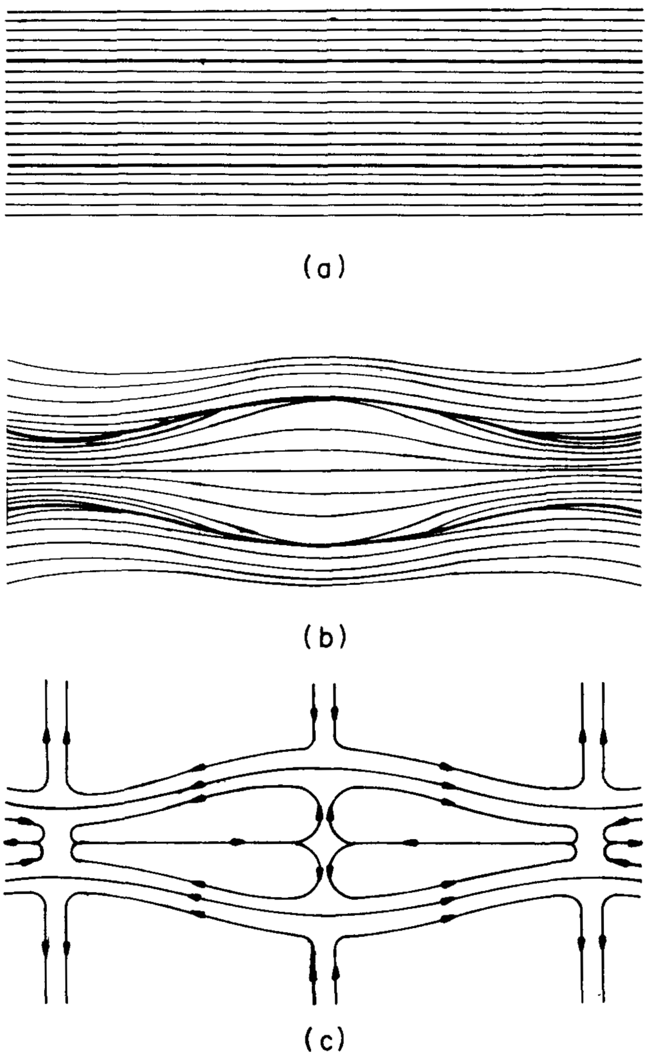

Fig. 6. Schematic diagram showing the influence of the Marangoni effect on jet stability. (a) Undeformed jet with lines indicating constant solute concentration. (b) Deformed jet showing distortion of constant solute concentration lines. (c) Internal flows set up by interfacial tension variations.

acterized by N_{EL}, on jet stability in the presence of mass transfer. Like the results in (I) the theory shows that the adsorption of the transferring solute itself will not have a significant effect (N_{EL} must be > 1000), but nontransferring surfactants may completely suppress either the stabilizing or destabilizing effects of the mass transfer.

Figure 8 shows the effect of the solute diffusivity in the surroundings on the dimensionless wave number of the most unstable disturbance. The physical situations described in Figure 8 are the same as those described in Figure 5. Comparison of Figures 5 and 8 shows that increasing $\bar{\beta}^*$ (decreasing jet length) is accompanied by increasing ξ^* (decreasing drop size) and vice versa except for large rates of transfer into the jet. In this case, increasing $\bar{\beta}^*$ is accompanied by decreasing ξ^* so that decreasing jet length is accompanied by increasing drop size. Of course, this behavior is only observed for situations with density and viscosity ratios greater than 0.85 ± .025 for the situations used for the present calculations.

Further consideration of the central physical example of Figures 2 to 5, 7, and 8 reveals more concerning the behavior of liquid jets in liquids with mass transfer. This example describes a situation where the density, viscosity, and diffusivity ratios are all equal to 1. from the previous study of Sternling and Scriven (1959) for planar liquid-liquid interfaces, such a situation produces a case of marginal stability, that is, a situation with no net Marangoni effect. It might at first seem logical to expect that the effective convection would be greater on the inside of

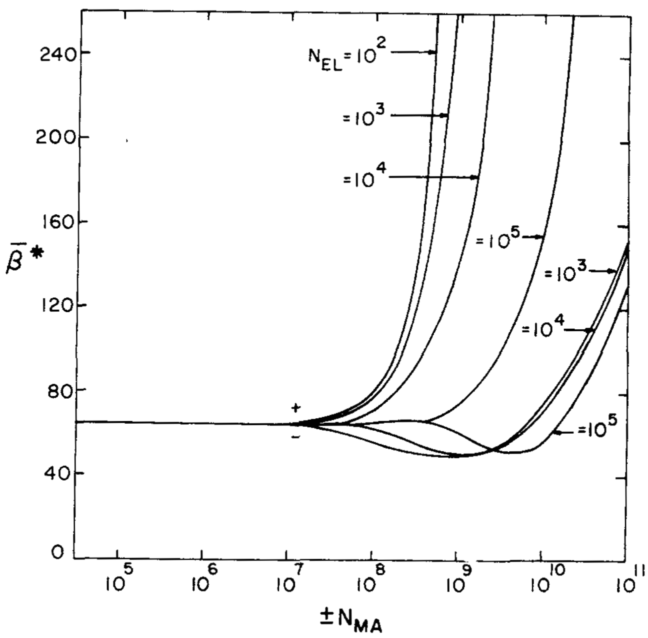

Fig. 7. Dimensionless growth constant vs. Marangoni number (+ and — denote sign of N_{MA}, $\hat{N}_{MA}$) showing the effect of mass transfer on jet stability in the presence of solute adsorption, as expressed by N_{EL}. Other dimensionless groups are set at $N_{SU} = 5 \times 10^4$, $N_{SS} = 0.04$, $N_{DN} = 1$, $N_{DF} = 1$, $N_{DI} = 1$, $N_{SC} = 10^3$.

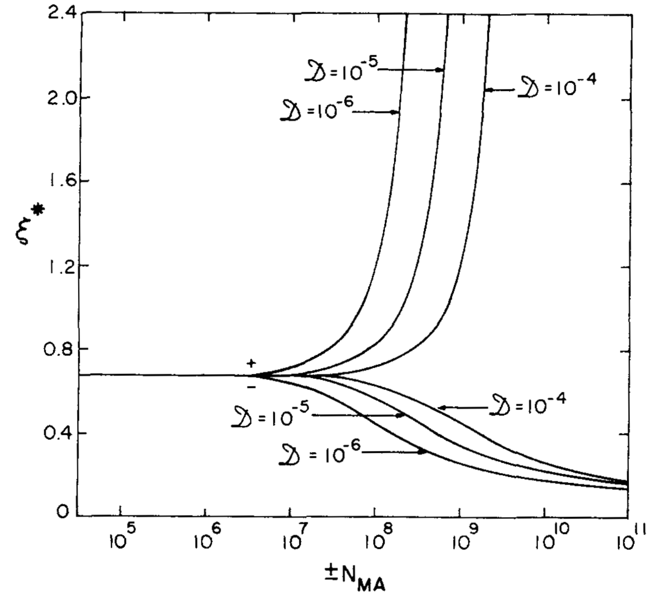

Fig. 8. Dimensionless wave number vs. Marangoni number (+ and — denote sign of N_{MA}) showing the effect of mass transfer on predicted drop size. Results are shown for various values of the diffusivity in the surroundings $\hat{D}$. Diffusivity inside the jet is set at $D = 10^{-5}$ cm²/s, $\hat{D}$ and $(\partial \hat{c}_0/\partial r)_a$ are varied simultaneously such that continuity of molar flux is maintained at the jet surface. Other dimensionless groups are set at $N_{SU} = 5 \times 10^4$, $N_{EL} = 0$, $N_{SS} = 0.04$, $N_{DN} = 1$, $N_{VS} = 1$, $N_{SC} = 10^3$.

the circular interface for cylindrical liquid-liquid systems, because the internal convection caused by a given interfacial tension gradient would be confined to very small volume while the external convection would be distributed over a much larger volume. Thus, transfer out of the jet might be expected to be stabilizing. However, because a cylindrical interface is being disturbed, the change in capillary pressure due to the dependence of surface tension on concentration ($(\partial\sigma/\partial c)c/a$ in the normal stress boundary condition) causes a local decrease in pressure at the disturbance peak which reinforces the convection in the surroundings such that the Marangoni convection actually becomes stronger on the outside of the disturbed circular interface. Thus, transfer out of the jet is actually destabilizing.

From the foregoing discussion it is clear that the consequences of the Marangoni effect for liquid jets in liquids are quite complicated. Thus, the development of simple criteria to predict, a priori, what Marangoni effect might be expected for a given physical situation is not possible, and qualitative effects cannot be predicted with certainty without the solution of Equation (13).

QUALITATIVE COMPARISON OF THEORY WITH EXPERIMENT

A qualitative comparison can be made between the present theory and the experimental results of Meister and Scheele for the transfer of acetone between benzene jets, directed vertically upward, and water. For the experiments with transfer into the jet, the water contained 5 wt. % acetone; for the experiments with transfer out of the jet, the benzene contained 5 wt. % acetone. The distribution coefficient in this system is approximately unity. Experimental results showed that mass transfer both in and out stabilized the jet (increased the jet length) relative to the no-transfer case of pure benzene jets in water, and mass transfer into the jet yielded longer jets than transfer out. While the general stabilization in the presence of acetone can be explained by lowered interfacial tension, the dependence on mass transfer direction was not explained. It is this effect that is to be examined in the context of the present theory.

Meister and Scheele's data for jet velocities of 35, 45, and 55 cm/s are shown in Table 2. Data for higher velocities cannot be used because of jet lengthening, which occurs when the jet velocity exceeds the drop rise velocity. It should also be noted that the Weber numbers corresponding to these experiments are below 5.3 so that aerodynamic effects (neglected in the present theory) would be expected to be negligible (Fenn and Middleman, 1969). To make the comparison, values for $\overline{\beta}^*$ are first calculated from the experimental data at each velocity. A value for η_0, the initial disturbance amplitude, is calculated from

$$\beta^* = \frac{U}{L}\ln\left(\frac{a}{\eta_0}\right) \qquad (14)$$

where β^* is the growth constant of the most unstable disturbance. This is accomplished using the theoretically predicted values of β^* for pure benzene jets in water and the measured values of U, L, and a from the experiments for the pure benzene-water system. Each η_0 value is assumed constant for all runs at that particular velocity. Thus, $\overline{\beta}^*$ values can be calculated from the measured jet lengths for each of the experiments of interest using the above equation and the definition of $\overline{\beta}^*$. The derived experimental $\overline{\beta}^*$ values are presented in Table 2.

TABLE 2. MEISTER AND SCHEELE DATA FOR THE ACETONE-BENZENE-WATER EXPERIMENTS AND THE EXPERIMENTAL $\overline{\beta}^*$ VALUES AND N_{MA} RANGES

Jet velocity, cm/s	Transfer situation	Jet length, cm	$\overline{\beta}^*$	N_{MA} range
35	No transfer	0.71	46.8	—
	Transfer out	0.97	34.2	1.6×10^6 to 6.0×10^7
	Transfer in	1.35	24.5	-1.6×10^6 to -1.0×10^8
45	No transfer	1.14	46.8	—
	Transfer out	1.46	36.6	1.6×10^6 to 6.0×10^7
	Transfer in	2.08	25.7	-1.6×10^6 to -1.0×10^8
55	No transfer	1.61	46.8	—
	Transfer out	1.94	38.8	1.6×10^6 to 6.0×10^7
	Transfer in	2.64	28.5	-1.6×10^6 to -1.0×10^8

The experimental situation is best described as penetration mass transfer into (or out of) a cylinder of initial solute concentration c_i from (or to) an infinite medium of initial solute concentration $\hat{c}_i$. Because the jet lifetimes for the experiments ($t = L/U$) are small ($\sim$ .04 s), the boundary layer thickness ($\delta_m \sim \sqrt{Dt}$) is small (0.0006 cm) relative to the jet radius (0.0405 cm), and the solute concentration profiles in both phases are strongly nonlinear. Hence, the jet itself may be considered an infinite medium. It is now clear that Sawistowski's explanation of Marangoni effects for liquid jets in liquids, which is based on the assumed quasi-equilibration between the two phases, cannot be applicable to the present situation. It is also clear that the assumption of linear undisturbed concentration profiles in both phases made in the theoretical derivation (primarily affecting the calculation of the Marangoni number) limits the comparison that can be made between theory and experiment to a qualitative one.

The interfacial concentration $(c_0)_a$ is calculated by $(c_0)_a = c_i/[1 + m\,(\hat{D}/D)^{1/2}]$ for transfer out of the jet and $(c_0)_a = \hat{c}_i/[m + (D/\hat{D})^{1/2}]$ for transfer into the jet. m was obtained from Meister and Scheele and D and $\hat{D}$ estimated by the method of Wilke and Chang (1955). The interfacial tension (σ) and its concentration coefficient ($\partial\sigma/\partial c$) are calculated from Meister and Scheele's data for the acetone-benzene-water system. Using Equation (13), theoretical $\overline{\beta}^*$ vs $\pm N_{MA}$ curves for the Meister and Scheele experiments are calculated using a series of assumed values for the concentration gradients in the jet and surroundings.

The calculation of the actual concentration gradients (necessary for the determination of N_{MA} and $\hat{N}_{MA}$) present in the experiments is necessarily arbitrary because the theory assumes they are linear while they are strongly nonlinear. The maximum value of $(\partial c_0/\partial r)_a$, (and hence the maximum Marangoni number) corresponding to the slope of the unsteady profile at the jet interface, is calculated as

$$\left(\frac{\partial c_0}{\partial r}\right)_a = -\frac{c_i}{\sqrt{\pi D t}}\,\frac{m(\hat{D}/D)^{1/2}}{1 + m(D/\hat{D})^{1/2}}$$

for transfer out of the jet and

$$\left(\frac{\partial c_0}{\partial r}\right)_a = \frac{\hat{c}_i/m}{\sqrt{\pi \hat{D} t}}\,\frac{(D/\hat{D})^{1/2}/m}{1 + (D/\hat{D})^{1/2}/m}$$

for transfer into the jet

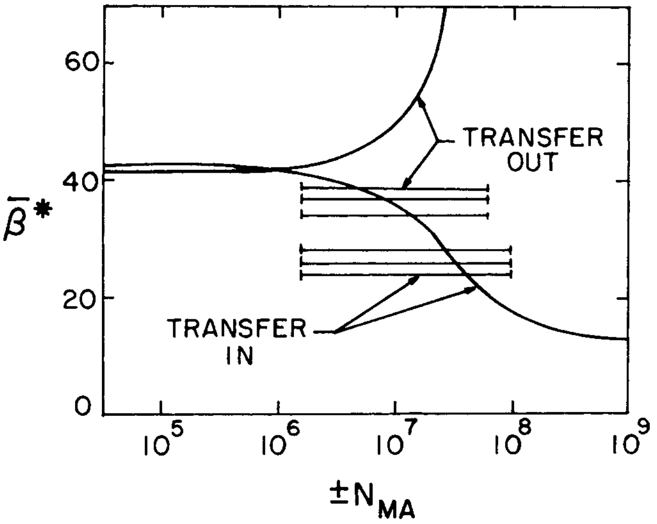

Fig. 9. Comparison of calculated growth constant vs. Marangoni number, shown as curved lines, with experimental results of Meister and Scheele (1969), as listed in Table 2.

The minimum value is calculated as

$$\left(\frac{\partial c_0}{\partial r}\right)_a = \frac{(c_0)_a - c_i}{a}.$$

Using both values defines the N_{MA} range shown in Table 2 and Figure 9.

Comparison of the data of Meister and Scheele with the predictions of the present theory is shown in Figure 9. The curves show the predicted dependence of the disturbance growth constant on mass transfer rate (expressed as N_{MA}) for transfer out and transfer into the jet under the conditions of the experiments. They show clearly that one should expect transfer out to yield shorter jets than transfer in. The sets of horizontal lines represent the data, with their lengths representing the range of N_{MA} values that might be assigned to each experimental condition. While the predicted absolute magnitudes of the growth constants are greater than those observed for both transfer directions, their relative magnitudes are in qualitative accord with experiment.

ACKNOWLEDGMENTS

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NOTATION

a = jet radius, cm
c = solute concentration disturbance, g-mole/cm^3
c_i = initial solute concentration, g-mole/cm^3
D = solute diffusivity, cm^2/s
h = number of axes of symmetry about which the disturbance oscillates, dimensionless
H_1 to H_{13} = defined in Equation (13)
$I_h(\ )$ = modified Bessel function of the first kind, order h
k = disturbance wave number, cm^{-1}
$K_h(\ )$ = modified Bessel function of the second kind, order h
L = jet length, cm
m = solute distribution coefficient
N_i = dimensionless groups defined in Equation (13)
p = pressure disturbance, dyne/cm^2
r = radial coordinate
R = gas constant
t = time, s
T = temperature, °K
u = velocity disturbance, cm/s
U = jet velocity, cm/s
z = axial coordinate

Greek Letters

β = growth constant, s^{-1}
$\bar{\beta}$ = dimensionless growth constant, $\beta \rho a^2/\mu$
Γ = solute adsorption, g-mole/cm^2
δ = adsorption equilibrium constant, cm
δ_m = mass transfer boundary layer thickness, cm
η = disturbance amplitude, cm
η_0 = initial disturbance amplitude, cm
θ = azimuthal coordinate
μ = viscosity, g/cm s
ν = kinematic viscosity, cm^2/s
ξ = dimensionless wave number
$\xi_1, \hat{\xi}_1, \xi_2, \hat{\xi}_2$ = defined in Equation (13)
ρ = density, g/cm^3
σ = surface tension, g/s^2

Subscripts

a, s = at the surface
i = initial
0 = undisturbed
r, z, θ = coordinates

Superscripts

$\wedge$ = surroundings
$*$ = most unstable

LITERATURE CITED

Burkholder, H. C., "The Effects of Surface Adsorption, Heat Transfer, and Mass Transfer on the Stability of Capillary Jets," Ph.D. dissertation, University of Washington, Seattle (1973).

Burkholder, H. C., and J. C. Berg, "The Effect of Mass Transfer on Laminar Jet Breakup: Part I. Liquid Jets in Gases," *AIChE J.*, **20**, 000 (1974).

Fenn, R. W., and S. Middleman, "Newtonian Jet Stability: The Role of Air Resistance," *AIChE J.*, **15**, 379 (1969).

Meister, B. J., "The Formation and Stability of Jets in Immiscible Liquid Systems," Ph.D. dissertation, Cornell Univ., Ithaca, New York (1966).

———., and G. F. Scheele, "Generalized Solution of the Tomotika Stability Analysis for a Cylindrical Jet," *AIChE J.*, **13**, 682 (1967).

———————., "Prediction of Jet Length in Immiscible Liquid Systems," *ibid.*, **15**, 689 (1969).

Rayleigh, Lord, "On the Instability of Jets," *Proc. London Math. Soc.*, **10**, 4 (1978).

———., "On the Capillary Phenomena of Jets," *Proc. Royal Soc. (London)*, **29**, 17 (1879).

———., "On the Instability of a Cylinder of Viscous Liquid under Capillary Force," *Phil. Mag.*, 34, 145 (1892).

Sawistowski, H., "Influence of Mass-Transfer-Induced Marangoni Effects on Magnitude of Interfacial Area and Equipment Performance in Mass Transfer Operations," *Chem. Ing. Tech.*, **45**, 1114 (1973).

Sternling, C. V., and L. E. Scriven, "Interfacial Turbulence: Hydrodynamic Instability and the Marangoni Effect," *AIChE J.*, **5**, 514 (1959).

Taylor, G. I., "Formation of Emulsions in Definable Fields of Flow," *Proc. Roy. Soc. (London)*, **A146**, 501 (1934).

Tomotika, S., "On the Instability of a Cylindrical Thread of a Viscous Liquid Surrounded by Another Viscous Liquid," *ibid.*, **A150**, 322 (1935).

Wilke, C. R., and P. Chang, "Correlation of Liquid Diffusion Coefficients," *AIChE J.*, **1**, 264 (1955).

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