values of the local Sherwood numbers for the second sphere are greater, due to the greater intensity of turbulent pulsations, caused by the presence and instability of the first wake.

These results indicate that, although mass transfer enhancement to the tube walls can be achieved by positioning an array of objects into the tube, the magnitude and distribution of local Sherwood numbers depends not only on *Re*, *l/d*, d/d_p (as found in previous work), but also on the type of objects used. The maximum and average Sherwood numbers are much higher in the case of two disks than for two spheres. Positioning of disks seems to be more favorable, not only because it yields higher mass transfer coefficients, but also because the pressure drop at an l/d_p ratio of 0.6 is smaller than the pressure drop in case of a single disk. Such effect cannot be achieved with spheres.

NOTATION

d = tube diameter
d_p = sphere diameter
l = distance between the spheres
Sh = local Sherwood number
Sh_∞ = local Sherwood number characteristic for undisturbed stream in the tube
x = distance along the tube

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Rectilinearity Rule for Vapor and Liquid Densities Along the Azeotropic Locus

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The phase behavior of mixtures at high pressures is of great practical as well as theoretical interest. Of particular note is the behavior of mixtures which deviate from ideality, to an extent that azeotropes are formed. Extensive work by Kay and coworkers (Kay and Brice 1953a, Kay and Rambosek 1953b, Skaates and Kay 1964) has shown that mixtures that form azeotropes in the critical region exhibit a minimum or maximum temperature point in their critical locus curves (Figure 1). On a P-T projection, the azeotropic locus becomes tangential to the critical locus curve at the critical azeotropic point. Because of this behavior, the co-ordinates of the critical azeotropic point are difficult to establish both theoretically (Teja and Kropholler 1974) and experimentally.

Azeotropic mixtures, however, exhibit certain characteristics which are typical of pure substances. For example, Licht and Denzler (1948) have shown that the logarithm of the azeotropic pressure is an approximately linear function of the reciprocal temperature. More recently, Li (1977) has shown that a given azeotropic mixture follows a rectilinear equation of the type:

$$\left(\frac{\rho^V_{az}+\rho^L_{az}}{2\rho^c_{az}}\right) = 1 + A\left(\frac{T_{az}-T^c_{az}}{T^c_{az}}\right) \qquad (1)$$

where ρ^V_{az}, ρ^L_{az}, and ρ^c_{az} are the saturation densities of the vapor phase, the liquid phase, and of the critical azeotrope, respectively. T_{az} is the azeotropic temperature, T^c_{az} is the critical azeotropic temperature and A is a constant. Li, however, went on to suggest that A for the azeotropes could be calculated from the slopes A_i of the rectilinear equations for the pure components as follows:

$$A = \Sigma\, x_i A_i \qquad (2)$$

where x_i is the "mole fraction of component i." It is not obvious which mole fraction is to be used, since this quantity varies along the azeotropic locus in Figure 1.

Equation (1) is a form of the so-called "Law of Rectilinear Diameters" proposed by Cailletet and Mathias (1886) to describe the behavior of the densities of the coexisting phases of a pure fluid, as a function of temperature near the gas-liquid critical point. Analogous rules for pure fluids have been proposed for the slopes of isochores issuing from the coexistence curve (Hall and Eubank 1976); the thermal conductivities of the coexisting phases of ammonia (Needham and Ziebland 1965), and the viscosities of coexisting phases of the low molecular weight n-alkanes (Starling et al. 1962).

An extension of the rectilinear diameter equation to the densities of coexisting phases of binary mixtures at constant temperature was proposed by Won and Prausnitz (1974) and is of the form:

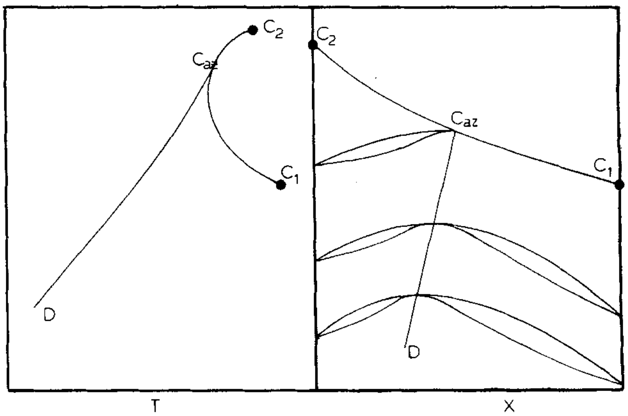

Figure 1. Schematic *P-T* and *P-x* diagrams for systems in which azeotropic behavior persists in the critical region. C_1, C_2 are the critical points of the pure components and C_{az} is the critical azeotropic point. The curve $C_1C_{az}C_2$ is the critical locus and the curve DC_{az} is the azeotropic locus.

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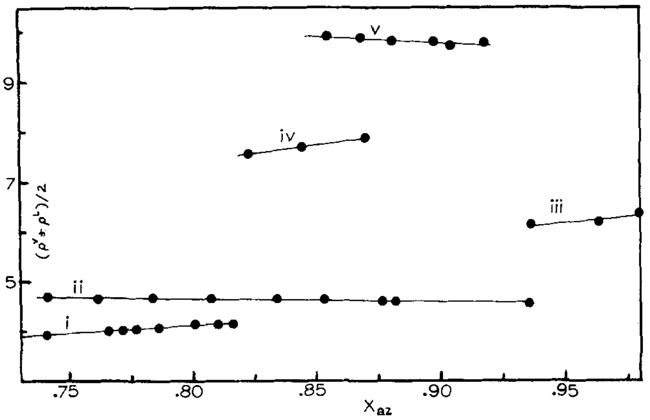

Figure 2. Mean density as a function of azeotropic composition. Roman numbers refer to the systems shown in Tables 1 and 2. For each system, x_{az} is the azeotropic composition (along the azeotropic locus) of the first-named component. The full circles are experimental points from the references cited in Tables 1 and 2.

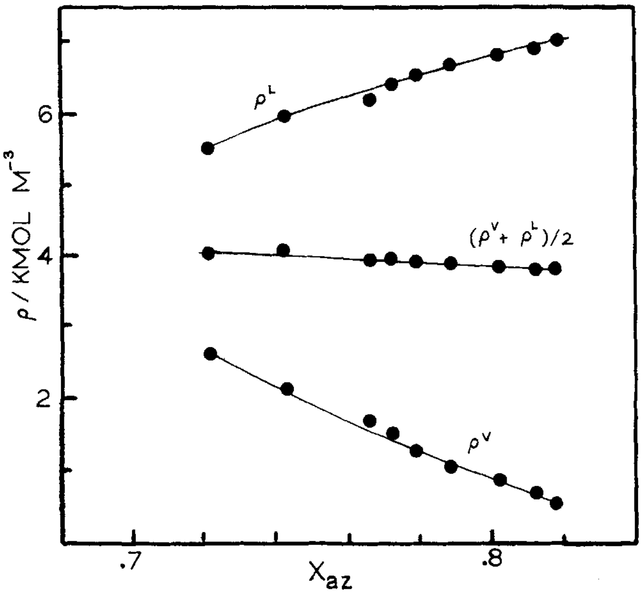

Figure 3. Rectilinear diameter for the Benzene-nButanol system.

$$\tfrac{1}{2}(\rho^V + \rho^G) = A' + B'P \tag{3}$$

where P is the pressure and A' and B' are constants.

No theoretical explanation of the law of rectilinear diameters is offered here. The extension of the law to densities along the azeotropic locus proposed below, however, was suggested by the behavior of the predicted densities using an extended form of the corresponding states principle (Teja and Rowlinson 1973).

A new rectilinear relationship, applicable to the densities of coexisting phases along the azeotropic locus, is proposed here. This relationship is of the form:

$$\tfrac{1}{2}(\rho^V_{az} + \rho^L_{az}) = A + B\, x_{az} \tag{4}$$

where x_{az} is the mole fraction of one of the components along the azeotropic locus and A and B are constants. When the azeotropic locus ends at a critical azeotropic point, Equation (4) may also be written as:

$$\left(\frac{\rho^V_{az} + \rho^L_{az}}{2\rho^c_{az}}\right) = 1 + C\left(\frac{x_{az} - x^c_{az}}{x^c_{az}}\right) \tag{5}$$

so that $A = \rho^c_{az} - B\, x^c_{az}$ and $B = C\, \rho^c_{az}/x^c_{az}$, where x^c_{az} is the mole fraction of one of the components at the critical azeotropic point. Equation (4) relates the densities of the coexisting phases to the composition of one of the components along the azeotropic locus. Each composition has associated with it a temperature and pressure (see Figure 1).

To illustrate Equation (4), mean densities for five binary mixtures that form azeotropes are shown as a function of azeotropic composition in Figure 2. For each of these mixtures, the P-T-x co-ordinates of the azeotropes are reported in the references cited in Table 1. Densities of the coexisting phases along dew and bubble point curves are also reported in the references. Cubic splines were fitted to these equilibrium curves and the densities at the azeotropic points were obtained by interpolation. Table 1 reports least squares constants A and B for Equation (4) when densities are in kmol m^{-3}. It is interesting to note that ethanol-benzene azeotropic mixtures appear to follow Equation (4), although the azeotropic locus for this mixture does not end at an azeotropic critical point, but rather at the vapor pressure curve of pure ethanol. Unfortunately, sufficient data are not available to reach a definite conclusion for azeotropic mixtures which do not have an azeotropic critical point.

A typical density-composition curve along the azeotropic locus is shown in Figure 3. The curve can be used to estimate the co-ordinates of the critical azeotrope. In this respect, the curve for ethanol-benzene azeotropes is similar, except that the vapor and liquid branches meet at mole fractions of ethanol greater than one. As demonstrated by Li (1977), equations such as (4) should prove useful for estimating saturation densities along the azeotropic locus when experimental data are incomplete.

Constants for the temperature-density relationship along the azeotropic locus of the form suggested by Li (1977)

TABLE 1. CONSTANTS FOR EQUATION (4).

System	A	B	SD	Corr. Coeff.	# of Data	Source
(i) Benzene-Butanol	1.6647	+3.0766	0.098	−0.992	9	Skaates (1964)
(ii) n Propanol-Benzene	5.2222	−0.6896	0.048	−0.913	9	Skaates (1964)
(iii) Ethanol-Benzene	1.3321	5.1023	0.128	0.867	3	Skaates (1964)
(iv) Ethane-H_2S	2.1935	6.5289	0.154	0.997	3	Kay (1953a)
(v) H_2S-Propane	6.6069	−2.8890	0.075	0.945	5	Kay (1953b)

TABLE 2. CONSTANTS FOR EQUATION (5).

System	A	$B \times 10^3$	SD	Corr. Coeff.	# of Data	Source
(i) Benzene-Butanol	7.8374	−7.09	0.098	−0.985	9	Skaates (1964)
(ii) n Propanol-Benzene	6.4859	−3.59	0.053	−0.917	9	Skaates (1964)
(iii) Ethanol-Benzene	−5.3860	23.80	0.127	0.931	3	Skaates (1964)
(iv) Ethane-H_2S	12.4612	−16.50	0.154	−0.998	3	Kay (1953a)
(v) H_2S-Propane	11.5643	−5.00	0.075	−0.959	5	Kay (1953b)

$$\tfrac{1}{2}(\rho^L_{az} + \rho^V_{az}) = A'' + B''T \qquad (6)$$

are given in Table 2. The magnitude of the correlation coefficient for the temperature-density relationship is similar to that for the composition-density relationship. (A value of the correlation coefficient close to ±1 indicates a high correlation between two variables and a value near 0 indicates low correlation. It is thus a measure of the "goodness of fit".) Once again, the data for ethanol-benzene azeotropes (when the azeotropic locus does not end at a critical azeotropic point for mole fractions between 0 and 1) can also be fitted to Equation (6), although there are insufficient data points to reach a definite conclusion.

In conclusion, the rectilinearity rule proposed by Cailletet and Mathias can be applied to saturation densities along the azeotropic locus, both as a function of temperature and of composition. The rule may have further applications to other properties of binary mixtures.

NOTATION

A, B, C = constants
P = pressure
T = temperature, K
x = composition
ρ = density, kmol m^{-3}

Superscripts

L = liquid
V = vapor
c = critical

Subscripts

i = component i
az = azeotrope

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Measurements of Turbulent Flow Velocity for Sudden Expansion Cylindrical Tube Using Laser Doppler Velocimeter (LDV)

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A laser Doppler velocimeter (LDV) is an apparatus for measuring frequency change of the scattered light (Doppler shift) from a particle moving inside a fluid. The Doppler shift is used to measure the velocity and the particle velocity is then used to infer the fluid velocity. A hot wire velocimeter has long been used for measuring a turbulent flow velocity, but the instrument has a drawback, in that it produces a disturbance inside the flow field. An LDV does not have the probe disturbance problem, because only light beams are passing through the flow field. Discussions of the LDV techniques can be found in the cited references.

In this study, an argon ion laser was used as a light source to measure the turbulent air flow velocity along the center line and radially, at certain cross sectional areas of a sudden expansion cylindrical tube. Results show that the center line velocity decreases to about 25% of the inlet velocity at a distance of about eight inlet diameters downstream ($X/D = 8$). A negative cross sectional velocity profile is observed at a distance of $X/D = 1.25$ from the tube entrance, which indicates that a circulation flow exists before the boundary layer reattachment.

EXPERIMENTAL APPARATUS

Flow System

A circular plastic tube 0.56m long, 101.6mm ID, and about 6.35mm thick was used as a test section. About 25.4mm thick and 152.4mm diameter circular plates, with a 50.8mm diameter hole at the middle of the plates, were attached co-axially to both ends of the 0.56m long tube. The back end of the tube was connected to a vacuum cleaner, and the air was sucked in through the 50.8mm diameter hole and expanded instantaneously to the 101.6mm ID plastic tube, (Figure 1). Baking soda

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