Rectilinear Diameter for Saturated Densities of Binary Mixtures

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Many years ago Cailletet and Mathias (1886) observed that for a pure fluid the arithmetic average of the densities of the saturated vapor and the saturated liquid is, to a close approximation, a linear function of the temperature; this observation is known as the law of rectilinear diameter. We wish to report here our observation that an analogous relation appears to exist for some binary mixtures: when the arithmetic average of the molar densities of the saturated vapor and the equilibrium saturated liquid is plotted against pressure at constant temperature, a nearly straight line is obtained.

In a two-phase binary mixture the two saturated phases at equilibrium have different compositions. We designate the mole fraction in the vapor y and that in the liquid x; the molar density is denoted by d with superscript L for liquid and superscript V for vapor. Our observation is that, at constant temperature,

$$\bar{d} \equiv \frac{1}{2}\,[d^L(x) + d^V(y)] = A + BP \qquad (1)$$

where P is the pressure and A and B are constants. It follows that

$$A = d_c - BP_c \qquad (2)$$

where subscript c refers to the critical state.

To illustrate Equation (1), mean densities for four binary systems are shown as a function of pressure in Figure 1. Point C is the critical point. The legend for Figure 1 is given in Table 1.

Table 2 reports least-square constants A and B when densities are given in g moles/liter and pressures in atmospheres. Also shown in Table 2 is the standard deviation in mean density between calculated and observed results.

No theoretical explanation for Equation (1) is readily apparent. However, Equation (1) may be useful for estimating saturated densities in binary mixtures when experimental data are incomplete or for estimating critical densities which are difficult to measure. To obtain an estimate of the critical density at a particular temperature it is necessary to specify saturated densities at pressures below the critical and the critical pressure corresponding to that temperature. Table 3 reports experimental critical volumes for three binary systems and those calculated by the method described above. Also shown in Table 3 are experimental critical pressures and the highest pressures used to determine the constants A and B. Agreement between predicted and experimental critical volumes is encouraging.

Figure 2 shows isothermal plots of saturated densities $d^V(y)$ and $d^L(x)$ versus pressure; the legend for Figure 2 is given in Table 4. The plots exhibit an ellipsoidal shape whenever the critical volumes of the solvent and solute are not excessively different [curves (1) and (2)]. However, if the difference in critical volumes is large, the curves exhibit an arrow shape [curve (6)] and at lower temperature, they may cross and then recombine at the critical point [curves (4) and (5)].

The mean densities give a more nearly straight line [Equation (1)] at higher temperature as indicated by the lower standard deviations given in column 5 of Table 2.

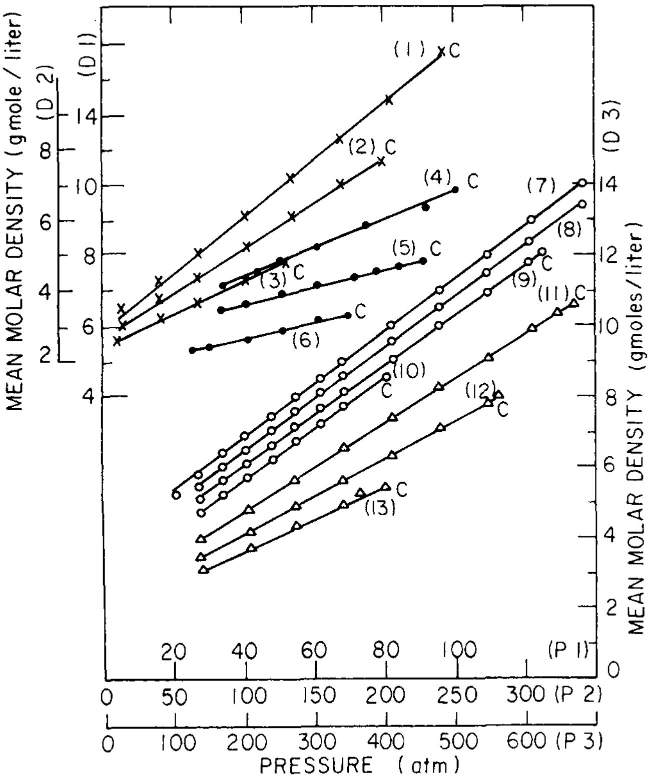

Fig. 1. Saturated mean density vs. pressure.

Table 1. Legend for Figure 1

Line	System	Temp., °C	Scale Density	Pressure
1, 2, 3	$CH_4 + nC_7H_{16}$	4.5, 71.1, 137.8	*D*2	*P*2
4, 5, 6	$CH_4 + C_3H_8$	4.5, 37.8, 71.1	*D*1	*P*1
7, 8, 9, 10	$H_2 + nC_6H_{14}$	104.5, 137.8, 171.1, 204.5	*D*3	*P*3
11, 12, 13	$CH_4 + nC_{10}H_{22}$	104.5, 171.1, 237.8	*D*3	*P*2

It appears that mixtures rich in a supercritical component deviate less from Equation (1) than do those where the mole fraction of the light component is small.

TABLE 2. SLOPE AND INTERCEPT OF RECTILINEAR DIAMETER AND STANDARD DEVIATION AT VARIOUS TEMPERATURES

System	Temp., °C	A^*	B^*	Std. dev.† (no. data points)	Data ref.
	171.1	3.30	14.0	0.96(12)	
Hydrogen	137.8	3.62	14.4	0.79(12)	Nichols
+	104.5	3.84	15.0	1.1(13)	et al.
n Hexane	71.1	4.19	15.3	1.5(13)	(1957)
	204.5	2.77	14.5	0.46(8)	
Methane	71.1	4.61	24.4	0.72(15)	Reamer
+	37.8	5.76	21.9	0.52(19)	et al.
Propane	4.5	5.86	38.4	0.71(20)	(1950)
Methane	71.1	3.01	31.2	1.4(15)	Reamer
+	104.5	2.76	24.5	1.1(14)	et al.
n Heptane	204.5	2.40	19.0	0.31(10)	(1956)
Methane	104.5	2.26	25.1	0.38(10)	Reamer
+	171.1	2.00	21.3	0.52(8)	et al.
n Decane	237.8	1.86	18.0	0.40(6)	(1942)

* A = g-mole/liter; $B = 10^{-3}$ g-mole/liter atm.

† Std dev: $100\sqrt{\Sigma\,(1 - \bar{d}\text{cal}/\bar{d}\text{exp})^2/(N - 2)}$

where $\bar{d}\text{exp} = \frac{1}{2}\,[d^L(x) + d^V(y)]$, $\bar{d}\text{cal} = A + BP$, and N = no. of data points.

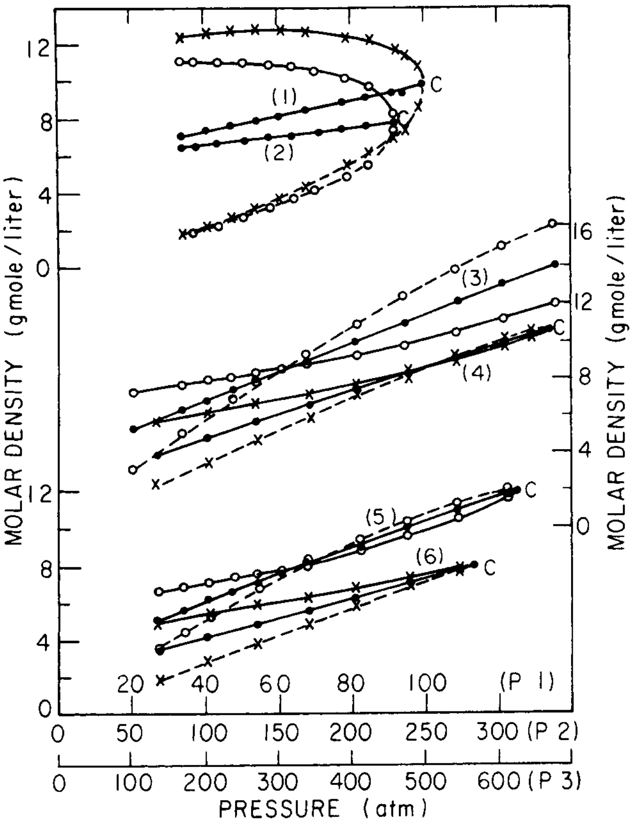

Fig. 2. Saturated density vs. pressure.

TABLE 3. COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED CRITICAL VOLUMES OF BINARY MIXTURE

System	Temp., °C	P_c(atm)	$P_{\max}$, no. of data points	V_c (cm^3/g-mole) Expt'l	V_c (cm^3/g-mole) Calc.	References
Argon + Neopentane	50	252	128.9(9)	88.5	87.9	Rogers and Prausnitz (1971)
Methane + Nonane	75	313	120(11)	88.0	90.9	
	50	318	120(11)	79.5	81.0	Shipman and Kohn (1966)
	25	319	140(12)	73.4	71.2	
Methane + Pentane	171.1	69.8	40.8(2)	229.8	230.0	
	137.8	109.6	68.1(6)	176.1	173.1	Sage et al. (1942)
	104.4	141.6	68.1(8)	141.0	138.5	
	71.1	159.1	85.1(9)	117.0	116.5	

ACKNOWLEDGMENT

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NOTATION

A, B = constants defined in Equation (1)
d = molar density, g mole/liter
$\bar{d}$ = mean molar density (g mole/liter), defined in Equation (1)
P = total pressure, atm
V = molar volume, cm^3/g mole
x, y = mole fractions of equilibrium liquid and vapor phases of binary mixture

Superscripts

L = liquid
V = vapor

Subscript

c = critical

TABLE 4. LEGEND FOR FIGURE 2

Curve no.	System	Temp., °C	Pressure scale
1	$CH_4 + C_3H_8$	4.5	*P*1
2		37.8	
4	$CH_4 + nC_{10}H_{22}$	104.5	*P*2
6		171.1	
3	$H_2 + nC_6H_{14}$	104.5	*P*3
5		171.1	

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Hydrodynamics and Mass Transfer for Suspended Solid Particles in a Turbulent Liquid

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Levins and Glastonbury (1972) presented an excellent review and analysis for mass transfer to particles suspended in an agitated fluid. They used Tchen's equation from Hinze (1959) for the prediction of particle-turbulent fluid relative velocity. The solution using the Gaussian error curve for the Lagrangian correlation function is shown to be

$$(u_R)^2{}_{\text{ave}} = \frac{2(1-b)^2}{\pi}\int_0^\infty \frac{\omega^2}{(a_1^2 + u_1^2)}\, T \exp - \frac{\omega^2 T^2}{\pi}\, d\omega \quad (1)$$

$$\omega_1 = \omega + c\sqrt{(\pi\,\omega/2)} \qquad a_1 = a + c\sqrt{(\pi\,\omega/2)}$$

$$b = 3\rho_f/(2\rho_s + \rho_f)$$

and for flow where Stokes law is applicable

$$a = \frac{36\,\mu}{(2\rho_s + \rho_f)d_p^2} \qquad c = \frac{18}{(2\rho_s + \rho_f)d_p}\sqrt{\frac{\mu\rho_f}{\pi}}$$

An analytic solution of Equation (1) is obtained by elimination of the Bassett term from Tchen's basic equation of motion which corresponds to $c = 0$. Levins and Glastonbury also report experimental data for fluid and particle velocities and the Lagrangian integral scales for a 25-cm diameter vessel with 7.5- and 10-cm diameter impellers. It was also observed that there were no significant differences between the root mean square fluctuating velocities of dense particles and the fluid which is consistent with the solution of the equation of motion of a particle in a turbulent fluid using the experimental Lagrangian scales of turbulence.

The objective of this paper is to utilize the Levins and Glastonbury work to develop a turbulent model for particle-liquid motion and mass transfer.

PARTICLE-LIQUID MOTION

Schartzberg and Treybal (1968) report mean and fluctuating velocities for several different impeller and vessel diameters that correlate as a function of $ND^2/(\overline{T}^2H)^{1/3}$ which corresponds to $(\epsilon D)^{1/3}$. The experimental data for fluctuating velocity reported by Levins and Glastonbury also are a function of the $(\epsilon D)^{1/3}$ term and are represented by

$$u_i = (\epsilon D)^{1/3}/3 \quad (2)$$

The Lagrangian integral scale data indicate that the length scale is approximately the width of the impeller and that the time scale can be approximated by

$$T = \frac{3\,D_i}{(\epsilon D)^{1/3}} \quad (3)$$

The a and c terms of Equation (1) represent Stokes law conditions. A more general equation for a is proposed by Schwartzberg and Treybal:

$$a = \frac{3\rho_f\, C_D\, u_R}{2(2\rho_s + \rho_f)d_p}$$

The c term can also be modified by replacing the drag coefficient response for Stokes law conditions with the drag coefficient. This results in the equation

$$c = \frac{3.67\,\rho_f}{(2\rho_s + \rho_f)}\sqrt{\frac{C_D\, u_R}{\pi\, d_p}}$$

which reduces to the c term of Equation (1) for $C_D = 24/N_{Re}$ corresponding to Stokes law conditions.

Zwietering (1958) presents correlations for suspension of sand and sodium chloride particles in low viscosity liquids with agitation conditions that are similar to those used by Levins and Glastonbury. If the minimum agitation conditions for particle suspension are assumed to