1. Although flow pulsations can generate significant changes in the instantaneous dispersion coefficient, they do not greatly increase axial mixing. That is, unless the amplitude of the fluctuations in the pressure gradient is greater than about one half of the mean pressure gradient, the time averaged dispersion coefficient is not more than 10% greater than the steady flow dispersion coefficient.
2. Changing the frequency of pulsation does not affect axial dispersion as much as changing the pulsation amplitude, and the time averaged unsteady flow dispersion coefficients increase slightly with decreasing frequency.

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NOTATION

d = diameter
G_s = dimensionless steady component of the pressure gradient
G_u = dimensionless amplitude of the unsteady component of pressure gradient
k = dimensional unsteady flow dispersion coefficient
k_s = dimensional steady flow dispersion coefficient
$\bar{k}$ = the time averaged unsteady flow dispersion coefficient
m = frequency
m' = dimensionless frequency (mR^2/ν)
p = dimensionless pressure
R = radius
N_{Re_s} = steady flow Reynolds number or time mean Reynolds number for unsteady flow
N_{Sc} = Schmidt number
u_0 = steady flow mean velocity or time mean bulk velocity
V_{amp} = velocity amplitude
z = dimensionless axial coordinate
θ = $2\pi m'\tau$
ν = kinematic viscosity
τ = dimensionless time

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Investigation into Reduced Property Correlations for Aliphatic and Aromatic Aldehydes

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The effect of pressure on the viscosity of liquids has been studied extensively for many years because of the importance of such data to the engineering and to the fundamental study of the liquid state. A number of investigators have studied pressure dependence for a variety of dense gases and liquids (*1* to *11*, *13*, *14*, *17* to *20*), which, coupled with simultaneous or independent investigations on the PVT behavior at high pressures, form the base of correlation procedures currently available.

During the course of this investigation, viscosity behavior of seven aliphatic and three aromatic aldehydes was established. The equipment was designed to provide for simultaneous measurement of fluid density. The details of the equipment, as well as the data obtained, have been presented elsewhere (*8*). The pressure range investigated was 0 to 20,000 lb./sq.in. gauge. The precision of pressure measurement was ±0.2%. The temperature was measured to an accuracy of 1/2°F. The viscosity values were estimated to be correct to within ±1%.

One method of correlating viscosity behavior of liquids with respect to pressure is due to Thodos and co-workers (*12*, *21*). Following the Abas-Zades (*12*) correlation procedure for thermal conductivities, Thodos et al. have developed similar correlations for residual viscosity. In this approach, residual viscosity $\mu - \mu_0$ is considered to be a function of the critical and physical parameters of a substance:

$$\mu - \mu_0 = \alpha\, T_c^a\, P_c^b\, v_c^c\, R^d\, M^e\, v^f \qquad (1)$$

By dimensional analysis, the following reduced property correlation results:

$$(\mu - \mu_0)\,\xi = \beta\, Z_c^m\, \rho_R^n \qquad (2)$$

For the data considered in the original Thodos' investigation, the correlation is shown by solid lines in Figure 1.

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Table 1. Calculated Values for Viscosity Parameter, Critical Compressibility Factor, and Constants for Equations (3)

Compound	Z_c	ξ	n	$-\ln \beta$
Acetaldehyde	0.2423	0.0291	17.1747	30.6541
Propionaldehyde	0.2561	0.0285	29.9416	46.3898
n-Butyraldehyde	0.2563	0.0288	23.6049	37.8362
iso-Butyraldehyde	0.2672	0.0282	23.2746	36.9446
iso-Valeraldehyde	0.2639	0.0285	24.0458	37.9734
Heptaldehyde	0.2497	0.0297	32.3859	48.1011
Caprylic aldehyde	0.2557	0.0299	36.2566	52.5764
Benzaldehyde	0.2621	0.0373	46.2594	64.3619
Anisaldehyde	0.2394	0.0213	60.7911	80.4371
trans-Cinnamaldehyde	0.2395	0.0251	59.3451	81.1111

Also shown in Figure 1 are recently reported viscosity data for methane and propane (*11*), *n*-butane (*9*), carbon dioxide (*13*), and argon, krypton, and xenon (*17*). The data points for nitrogen (*13*), while not so recent, have been included since they were not considered in the original correlation. The data for ammonia (*6*) and sulfur dioxide (*20*) were considered by Stiel and Thodos and pointed out as not obeying the general trend. They are included in Figure 1 merely to indicate the extent of their departure from the correlation. It can be concluded that Thodos' correlation is highly satisfactory for a large number of substances but should not be used for substances like carbon dioxide and sulfur dioxide. The predictive accuracy of Thodos' correlation is, in general, better for ρ_R from one to three rather than for ρ_R less than one, as can be seen from Figure 1.

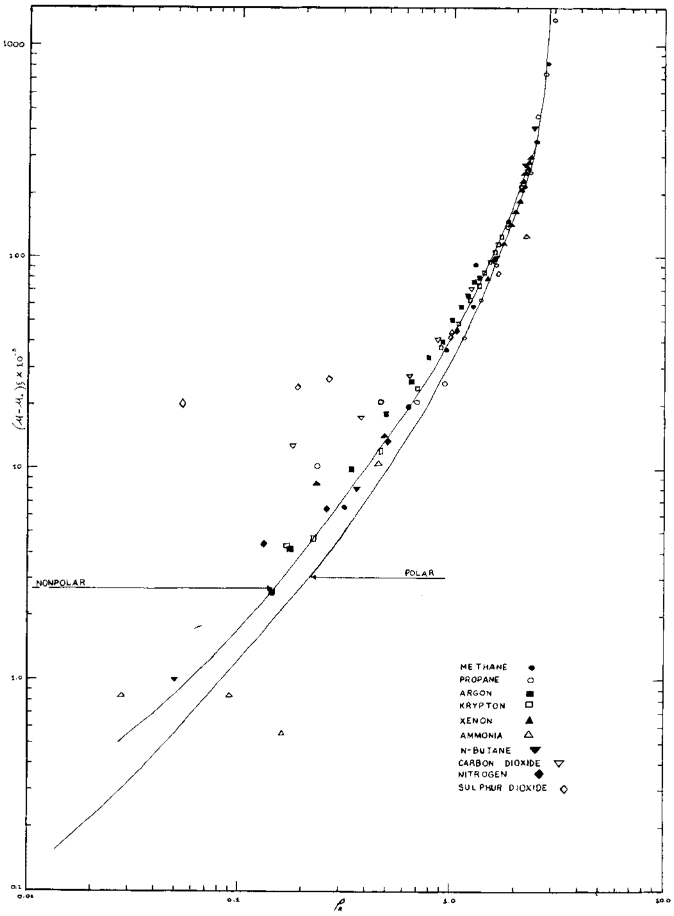

Fig. 1. The Thodos correlation.

In order to develop reduced density correlations for aldehydes, it was first necessary to establish the critical properties of the substance for which such data are not available. The critical properties were estimated by methods involving the least quoted errors. The Reidel-Guldberg method (*16*) was used for critical temperature, while the Lynderson method (*15*) was utilized for critical pressure and volume. The calculated ξ and Z_c values are presented in Table 1. The errors in prediction of critical temperature, pressure, and volume are believed to be less than 2, 5, and 5%, respectively. The values of $(\mu - \mu_0)\ \xi$ are plotted against reduced density in Figure 2, on which Thodos' correlation is also shown for comparison purposes. The range of aldehyde data is, of course, outside the range of Thodos' correlation. The trend shown by the aldehyde data is also, however, different from what one might expect by extrapolation of Thodos' correlation. The aldehyde data therefore raise the interesting possibility that reduced property correlations may exhibit a sharp discontinuity around $\rho_R \approx 3.0$. Development of a fully generalized reduced density correlation for liquids under high pressure will have to await more comprehensive viscosity-density data than are currently available. It seems certain, nonetheless, that a liquid state correlation will call for refinements in approaches used thus far, since the sensitivity of viscosity to density changes is much different for gaseous and liquid states.

From the nature of the aldehyde curves in Figure 2, it appears that an equation of the same form as Equation (2) may provide a satisfactory correlation for those substances. Equation (2), without the Z_c dependence, can be rewritten as

$$\ln (\mu - \mu_0)\ \xi = n \ln \rho_R + \ln \beta \tag{3}$$

Linear regression resulted in the following correlation:

$$\ln (\mu - \mu_0)\ \xi = 32.9375 \ln \rho_R - 48.5658 \tag{4}$$

Equation (4) is, however, not quite satisfactory since confidence level for the correlation is below 95%. In order to detect trends in the values of parameters β and n, Equation (4) was fitted independently for each aldehyde. The resulting parameter values are shown in Table 1. It was found that parameters β and n for aliphatic aldehydes (with the exception of propionaldehyde) can be expressed empirically as following functions of molecular weight:

$$\begin{aligned} \beta &= \exp\,(-19.5 - 0.25\ M) \\ \mathrm{n} &= 7.0 + 0.22\ M \end{aligned} \tag{5}$$

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NOTATION

m = constant, Equation (2)
M = molecular weight
n = constant, Equation (2)
P_c = critical pressure, atm.
R = gas constant
T_c = critical temperature, °K.
v = molar volume, cc./g.-mole
v_c = critical molar volume, cc./g.-mole
Z_c = critical compressibility factor

Greek Letters

α = constant, Equation (1)
β = constant, Equation (2)
μ_0 = viscosity at normal pressure, cp.
ξ = viscosity, cp.

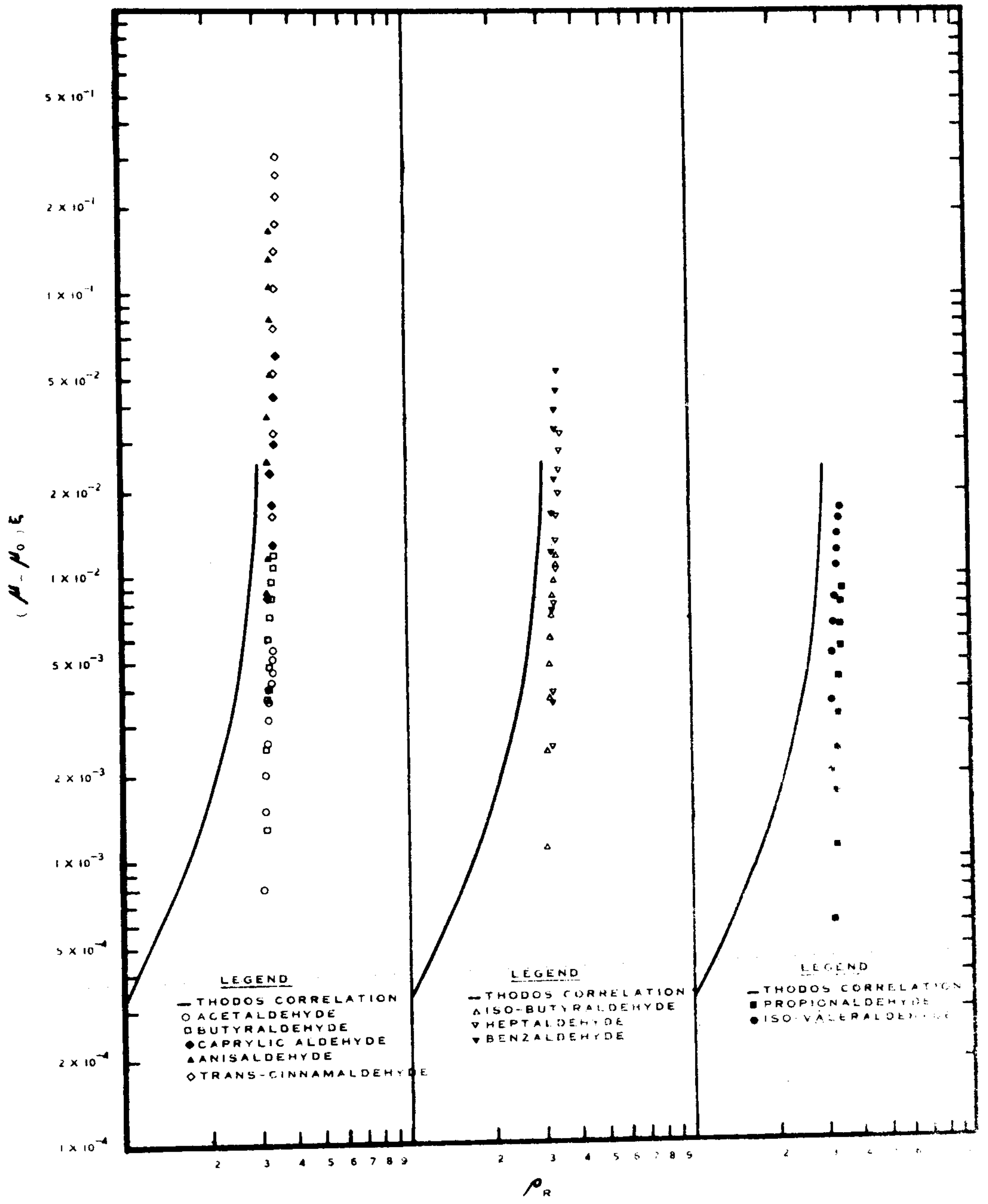

Fig. 2. The Thodos correlation compared to aldehyde data.

μ = viscosity parameter: $T_c^{1/6}/M^{1/2}\,P_c^{2/3}$

ρ_R = reduced density

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