Thermal Pressure Applied to the Prediction of Viscosity of Simple Substances in the Dense Gaseous and Liquid Regions

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The reduced thermal pressure-temperature ratio has been used to relate residual viscosity modulus for argon, krypton, and xenon into a unique relationship applicable for the dense gaseous and liquid regions. For these monatomic substances the critical compressibility factor is $z_c = 0.291$. Values of $(\partial P_R/\partial T_R)_{\rho_R}$ vs. $(\mu - \mu^*)\xi$ on log-log coordinates produced a linear relationship. For these simple substances, this relationship was used to predict viscosities with an average deviation of 3.0% for fifty eight experimental values. This relationship was also applied for the prediction of viscosities for nitrogen, oxygen and carbon dioxide.

The approach developed in this study merits further examination with several additional substances. The lack of adequate thermal pressures in the dense gaseous and liquid regions of substances other than argon limits the use of this study to substances having critical compressibility factors $z_c = 0.291$.

The effect of pressure on the viscosity of substances in the dense gaseous and liquid regions has been represented by a relationship between the residual viscosity $\mu - \mu^*$ and ρ, the density. Experimental viscosities of gases at elevated pressures and of the liquid state have been utilized to produce individual relationships of $\mu - \mu^*$ vs. ρ for argon (*20*), nitrogen (*1*), oxygen (*1*), hydrogen (*1*), carbon dioxide (*10*), ammonia (*6*), and water (*23*). Each of these relationships was found to be continuous when extended from the gaseous state to the liquid state. Using a dimensional analysis approach, Thodos and co-workers (*9, 22*) have consolidated these individual relationships for polar and nonpolar substances into a single continuous curve by relating the quantity $(\mu - \mu^*)\ \xi$ to ρ_R, the reduced density. Water was not included because it exhibits an abnormal behavior, which may be due to its excessive hydrogen bonding effects. The viscosity parameter ξ has been shown to be $\xi = T_c^{1/6}/M^{1/2}P_c^{2/3}$ from dimensional analysis. The $(\mu - \mu^*)\ \xi$ vs. ρ_R relationship is unique and exhibits a high dependence on density, especially in the liquid state. The complex nature of this function has required the use of a fourth-degree polynomial for its description over the complete range of the gaseous and liquid states (*9*).

In view of the high dependence of $(\mu - \mu^*)\ \xi$ on reduced density, it would prove advantageous to introduce a thermodynamic quantity comparable to density which might provide a simpler functional relationship with $(\mu - \mu^*)\ \xi$, the residual viscosity modulus.

THERMAL PRESSURE

From an elementary type of treatment, it is possible to show that the van der Waals' equation of state

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \qquad (1)$$

can produce the following expression:

$$T\left(\frac{\partial P}{\partial T}\right)_v = P + \frac{a}{v^2} \qquad (2)$$

Equation (2) states that the sum of the external pressure P and the internal pressure a/v^2 is equal to the quantity $T(\partial P/\partial T)_v$, which, according to Hirschfelder, Curtiss, and Bird (*7*), is defined as the *thermal pressure.*

For the general case, the PVT behavior can be expressed in terms of a virial type of equation of the form

$$\frac{Pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \ldots \qquad (3)$$

where $B(T)$, $C(T)$, . . . are temperature dependent virial coefficients.. For a rigid sphere model, these virial coefficients are temperature independent, and differentiation of Equation (3) with respect to temperature, results in

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}\left[1 + \frac{B}{v} + \frac{C}{v^2} + \ldots\right] \qquad (4)$$

Table 1. Basic Constants and Average Deviations of Viscosity for Six Simple Substances

	z_c	ρ_c, g./cc.	ξ	State	Number of points	Average deviation, %	Source
Argon	0.291	0.536	0.02751	dense gas	10	1.8	(*15*)
				dense gas	20	5.8	(*18*)
				liquid	8	10.6	(*24*)
Krypton	0.291	0.908	0.01859	dense gas	20	1.4	(*18*)
Xenon	0.290	1.099	0.01505	dense gas	20	2.1	(*18*)
Nitrogen	0.291	0.311	0.04071	dense gas	12	1.3	(*17*)
				dense gas	4	1.6	(*8*)
Oxygen	0.293	0.410	0.03014	dense gas	9	8.3	(*13*)
Carbon dioxide	0.275	0.467	0.02242	dense gas	14	7.1	(*16*)

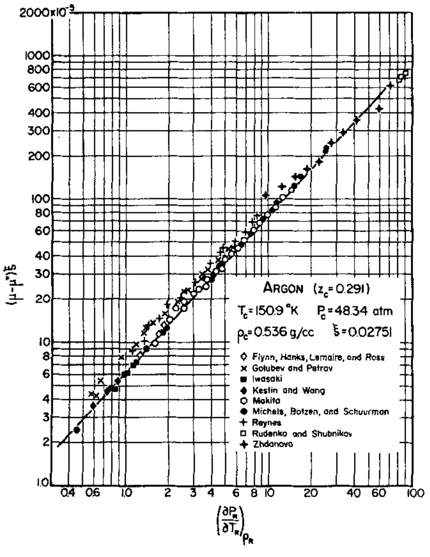

Fig. 1. Relationship between $(\mu - \mu^*)\xi$ and $(\partial P_R/\partial T_R)_{\rho R}$ for argon.

Then multiplication of both sides of Equation (4) by T yields

$$T\left(\frac{\partial P}{\partial T}\right)_v = \frac{RT}{v}\left[1 + \frac{B}{v} + \frac{C}{v^2} + \ldots\right] \quad (5)$$

Thus, it can be seen that for a rigid sphere model, the external pressure P of Equation (3) is equivalent to the thermal pressure

$$P = T\left(\frac{\partial P}{\partial T}\right)_v \quad (6)$$

This deduction is consistent with that stated by Hirschfelder, Curtiss, and Bird (*7*). Upon differentiation of the general gas law relationship $Pv = zRT$, it follows that

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{M}\rho\left[z + T\left(\frac{\partial z}{\partial T}\right)_v\right] \quad (7)$$

Equation (7) indicates that a direct correspondence exists between density and $(\partial P/\partial T)_v$, the thermal pressure-temperature ratio. Smith (*21*) has shown that a correspondence between density and the quantity $(v/R)(\partial P/\partial T)_v$ does exist for the liquid state. The present investigation attempts to utilize the quantity $(\partial P/\partial T)_v$ in place of density for the correlation of the residual viscosity of gases at high pressures and liquids.

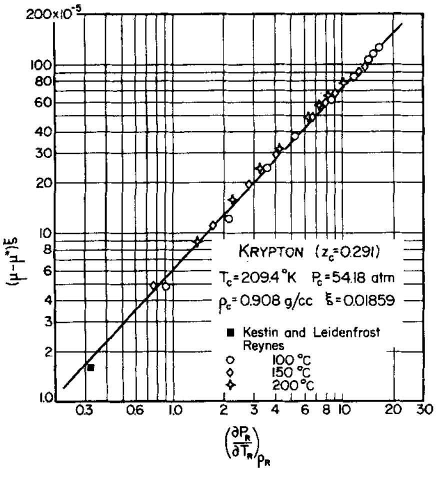

Fig. 2. Relationship between $(\mu - \mu^*)\xi$ and $(\partial P_R/\partial T_R)_{\rho R}$ for krypton.

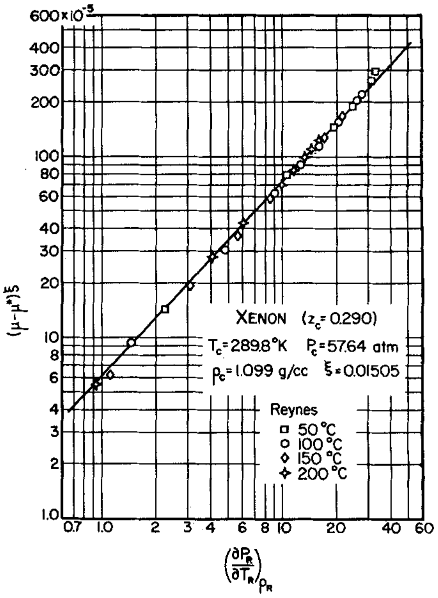

Fig. 3. Relationship between $(\mu - \mu^*)\xi$ and $(\partial P_R/\partial T_R)_{\rho R}$ for xenon.

TREATMENT OF EXPERIMENTAL VISCOSITY DATA

Attempts to correlate the residual viscosity $\mu - \mu^*$ with the thermal pressure-temperature ratio have been put forth in Russian literature by Golubev (*4*). In his work Golubev has considered only the dense gaseous region and has produced on log-log coordinates individual plots for a few substances.

A dimensional analysis approach which considers the residual viscosity as a function of the basic constants of a substance and the thermal pressure-temperature ratio suggests

$$\mu - \mu^* = f[(\partial P/\partial T)_v, T_c, P_c, v_c, R, M] \quad (8)$$

which produces the relationship

$$(\mu - \mu^*)\xi = \frac{\alpha}{R^{1/6}} z_c^{\,m} \left(\frac{\partial P_R}{\partial T_R}\right)_{\rho R} \quad (9)$$

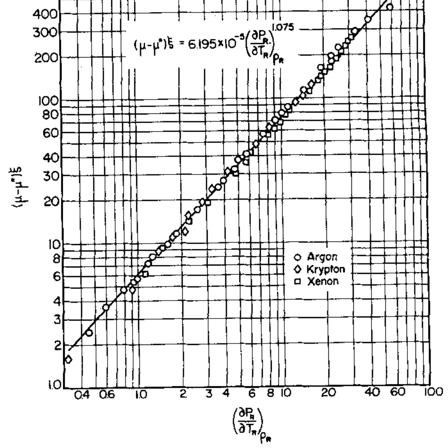

Fig. 4. Combined relationship between $(\mu - \mu^*)\xi$ and $(\partial P_R/\partial T_R)_{\rho R}$ resulting from viscosity data for argon, krypton, and xenon.

A comprehensive study of Equation (9) is beyond the scope of this investigation because of the lack of sufficient PVT data for different substances to cover the regions for which experimental viscosities exist. A thorough investigation of the thermal pressure to cover substances of all types over a wide range of temperatures and pressures, including the gaseous and liquid states, becomes a major study in itself. Consequently, in this study, it became necessary to limit the substances to be investigated to those for which thermal pressure values can be readily obtained.

The results of a recent study by Damasius and Thodos (*2*) on a generalized correlation of the Enskog modulus $b\rho\chi$ with reduced temperature and reduced pressure can be used for the calculation of values of $(\partial P_R/\partial T_R)_{\rho_R}$ for substances whose critical compressibility factors are $z_c \approx 0.291$. This correlation was developed from PVT data for argon. It was shown in their study that the Enskog modulus can be expressed in terms of reduced variables as

$$b\rho\chi = \frac{z_c}{\rho_R}\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} - 1 \qquad (10)$$

Consequently, for a selected reduced temperature and reduced pressure, the reduced thermal pressure-temperature ratio $(\partial P_R/\partial T_R)_{\rho_R}$ can be calculated from Equation (10). Existing viscosity data for the dense gaseous region for argon, krypton, and xenon and for the liquid state for argon were used to calculate the quantity $(\mu - \mu^*)\xi$, which was then correlated with the corresponding value of $(\partial P_R/\partial T_R)_{\rho_R}$. In order to produce the group $(\mu - \mu^*)\xi$ atmospheric pressure viscosities were obtained from the work of Shimotake and Thodos (*20*); the values of ξ used are presented in Table 1.

Experimental viscosities for argon were obtained from nine different sources. Although the majority of the data are for the dense gaseous region, sufficient experimental viscosities exist for the liquid state to enable a comprehensive consideration of both phases. Experimental argon viscosities used for the dense gaseous region were those of Iwasaki (*8*); Flynn, Hanks, Lemaire, and Ross (*3*); Golubev and Petrov (*5*); Reynes (*18*); Michels, Botzen, and Schuurman (*15*); Kestin and Wang (*12*); and Makita (*14*). For the liquid state, the experimental argon viscosities reported by Rudenko and Shubnikov (*19*) and Zhdanova (*24*) were used. The resulting plot of $(\mu - \mu^*)\xi$ vs. $(\partial P_R/\partial T_R)_{\rho_R}$ for argon is presented on log-log coordinates in Figure 1. With the exception of points calculated from the data of Golubev and Petrov (*5*) and Reynes (*18*), the points follow a straight line which includes both the gaseous and liquid states.

Although considerable viscosity data exist for argon, hardly any other high-pressure data for krypton and xenon existed prior to the work of Reynes (*18*). For krypton, the only other available data are those of Kestin and Leidenfrost (*11*), who report values for pressures up to 21 atm. The experimental viscosities of Reynes for krypton were measured at 100°, 150°, and 200°C. for pressures up to 12,045 lb./sq. in. abs. The resulting relationship between $(\mu - \mu^*)\xi$ and $(\partial P_R/\partial T_R)_{\rho_R}$ is presented in Figure 2 for krypton. Likewise, the only high-pressure experimental viscosities available for xenon are those of Reynes (*18*), who established values at 50°, 100°, 150°, and 200°C. for pressures up to 12,045 lb./sq. in. abs. The relationship resulting from points calculated from Reynes' experimental viscosities for xenon are presented in Figure 3.

APPLICATION OF CONSOLIDATED RELATIONSHIP TO OTHER SUBSTANCES

The linear relationships of Figures 1, 2, and 3 are essentially identical and can be combined into the single relationship presented in Figure 4. This relationship can be expressed analytically as follows:

$$(\mu - \mu^*)\xi = 6.195 \times 10^{-5}\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R}^{1.075} \qquad (11)$$

Equation (11) has been used to calculate viscosities for the substances used to develop this equation. In this regard viscosities calculated for argon in the dense gaseous region were compared with corresponding experimental values from the extensive and reliable work of Michels, Botzen, and Schuurman (*15*). For ten arbitrarily selected values, the average deviation was found to be 1.82%. For the liquid state of argon, experimental viscosities are somewhat erratic, and consequently the residual viscosities derived from them exhibit some positive and negative deviations from the straight line of Figure 4. Eight experimental values from the work of Zhdanova (*24*) were compared with calculated values to produce an average deviation of 10.6%. The significant positive and negative deviation of residual viscosity suggest that additional viscosities be established experimentally for the liquid region of argon and/or krypton and xenon. For krypton and xenon, twenty experimental viscosities of each substance in the dense gaseous region were compared with corresponding calculated viscosities to give an average deviation of 1.4% for krypton and 2.1% for xenon. This information is summarized in Table 1.

The application of the relationship of Figure 4 was extended to include simple substances other than argon, krypton, and xenon. For nitrogen in the dense gaseous state, a total of sixteen viscosity values from the work of Michels and Gibson (*17*) and Iwasaki (*8*) produced an average deviation of 1.4%. For oxygen, nine experimental values for the dense gaseous state from the work of Kiyama and Makita (*13*) produced an average deviation of 8.3%. This greater deviation may be due to the paramagnetic nature exhibited by oxygen. Similarly, fourteen experimental values for the dense gaseous state of carbon dioxide from the work of Michels, Botzen, and Schuurman (*16*) yielded an average deviation of 7.1%. These results for nitrogen, oxygen, and carbon dioxide are presented in Table 1.

These comparisons indicate that the approach presented in this study for the estimation of residual viscosities is feasible and merits further investigation. The present limitations for a comprehensive evaluation of this method reside in the lack of adequate thermal pressures for substances other than argon (*2*). Until such a time when more extensive information dealing with this thermodynamic property becomes available, the application of the thermal pressure concept should be restricted to the conclusions of this study.

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NOTATION

a,b = constants for van der Waals' equation of state, Equation (1)
B, C = second and third virial coefficient, respectively, for rigid sphere model, Equation (4)
$B(T), C(T)$ = second and third virial coefficients, repectively, Equation (3)
M = molecular weight
P = external pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v = molecular volume, cc./g.-mole
v_c = critical volume, cc./g.-mole

z = compressibility factor, Pv/RT
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α = dimensionless constant, Equation (9)
μ = absolute viscosity, centipoises
μ^* = viscosity at normal pressures, centipoises
ξ = viscosity parameter, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c
$b\rho\chi$ = Enskog modulus

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The Influence of Mass Transfer on a Countercurrent Liquid-Liquid Fluidized System

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The present work is concerned with an experimental study of the influence of mass transfer on the holdup of countercurrent lqiuid-liquid fluidized systems and the effect of solute on droplet coalescence. Of particular importance in the results obtained is the dramatic demonstration that mass transfer greatly influences the holdup when solute is being extracted from the discontinuous phase loading to strong coalescence.

The prediction of the volume fraction of the discontinuous phase is of particular concern in fluidization studies. The recent development of a generalized theory of fluidization (*14*) has led to a means of carrying out such a prediction. In accordance with this theory the volume fraction of the discontinuous phase or the holdup of any fluidized system is dependent solely on the relative velocities of the slip velocity between the phases for a given set of fluid properties and a given geometry. The theory has been experimentally verified for all regimes of solid-liquid fluidization and a modification of the theory accounting for drop and bubble terminal velocities verified for countercurrent liquid-liquid (*1*, *23*) and gas-liquid systems (*3*). This modified theory states that the holdup is a function of the slip velocity-terminal velocity ratio where the added factor of a terminal velocity is defined for an average size drop or bubble. Apparently, drop and bubble motion which might cause a departure from ideal solid sphere behavior does not influence the fluidized system to any measurable degree.

Many observations on the behavior of liquid-liquid extraction systems indicate that solute transfer between the