The Viscosity of Polar Gases at Normal Pressures

LEONARD I. STIEL and GEORGE THODOS

The Technological Institute, Northwestern University, Evanston, Illinois

The viscosity behavior at normal pressures (0.2 to 5 atm.) of fifty-three polar gases was examined, and equations representing the dependence of viscosity on temperature for these gases were developed. A dimensional analysis approach was applied to the variables effecting the viscosity of polar gases at moderate pressures. These variables were assumed to be the molecular weight, temperature, and the critical constants of the substance.

Reliable viscosity data available in the literature for the polar gases investigated were utilized to determine the exact dependence of their viscosities on these variables. In contrast to the results of a previous study, which show that for nonpolar gases the viscosity parameter $\mu^*\xi$ (where $\xi = T_c^{1/6}/M^{1/2}\,P_c^{2/3}$) is independent of z_c; the results of the present study indicate that for polar gases this parameter is dependent on z_c. The viscosity parameters of gases which exhibit hydrogen bonding were found to depend uniquely on $z_c^{5/4}$ and reduced temperature, while the remaining polar gases were found to exhibit a different unique dependence on $z_c^{2/3}$ and reduced temperature. For these two classes of polar substances separate viscosity relationships were developed.

For eleven gases which exhibit hydrogen bonding viscosities were calculated and compared with corresponding experimental values. An average deviation of 1.47% resulted from 129 experimental points. For the other polar gases the calculated values were also compared with experimental values and produced an average deviation of 2.59% for 197 experimental points.

Considerable attention has been directed to the development of relationships for the calculation of viscosities of gases at normal pressures. These relationships have been developed not only from the use of kinetic theory but also from the use of statistical mechanics and empirical approaches. The equations developed by these various methods are in general more reliable when applied to nonpolar gases than to polar gases, and none of them correctly predicts the behavior of gases which possess strong hydrogen bonding effects.

In 1944 Licht and Stechert (*14*), using the Sutherland equation and empirical estimations, developed the following relationship for the viscosity of gases at normal pressures:

$$\mu^*\xi = 63.0 \times 10^{-5}\frac{T_R^{3/2}}{T_R + 0.8} \quad (1)$$

where $\xi = T_c^{1/6}/M^{1/2}\,P_c^{2/3}$. Equation (1) gives good results for most nonpolar and slightly polar gases at moderate temperatures but gives poor results for several polar gases, particularly those which exhibit hydrogen bonding such as water, ammonia, and the alcohols (*27*).

Using a rigid sphere model and employing the Lennard-Jones potential function one obtains

$$F(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (2)$$

Hirschfelder, Curtiss, and Bird (*11*) developed for the viscosity of nonpolar gases at moderate pressures the relationship

$$\mu^* = 266.93 \times 10^{-5}\frac{\sqrt{MT}}{\sigma^2\,\Omega^{(2,2)*}[T_N]} \quad (3)$$

where ϵ and σ are the Lennard-Jones force constants and the collision integral $\Omega^{(2,2)*}[T_N]$ is a function of the normalized temperature $T_N = T/\frac{\epsilon}{\kappa}$. Bromley and Wilke (*6*), using the approximate relationships that $\epsilon/\kappa = 0.75\,T_c$ and $\sigma = 0.833\,v_c^{1/3}$, modified Equation (3) to obtain the following relationship for the viscosity of gases at moderate pressures:

$$\mu^* = 333 \times 10^{-5}\frac{\sqrt{M\,T_c}}{v_c^{2/3}}f(1.33\,T_R) \quad (4)$$

where values of $f\ (1.33\ T_R)$ are presented by them. Although in the development of Equations (3) and (4) it was assumed that the molecules possessed no polarity, these relationships have been applied with some degree of success to slightly polar compounds, but they fail to produce reliable viscosities for highly polar substances (*27*).

The Stockmayer potential should be used in the development of relationships for the transport properties of polar gases. This potential is represented by the sum of the Lennard-Jones potential and an angle dependent term accounting for the dipole interactions of two molecules:

$$F(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3}g(\vartheta,\varphi) \quad (5)$$

The maximum value $g(\vartheta,\varphi)$, the angular dependence of the dipole-dipole interaction, is 2. Krieger (*12*) assumed cigar shaped molecules whose charged ends are perfectly aligned with each other, and therefore $g(\vartheta,\varphi)$ is its maximum value, 2. Krieger used the resulting potential to develop collision integrals for Equation (3) which are

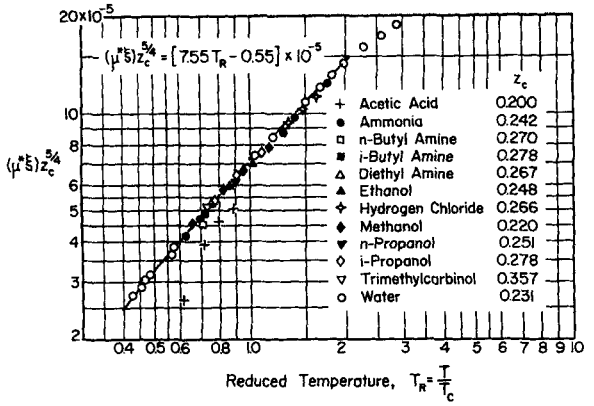

Fig. 1. Relationship between $(\mu^*\xi)z_c^{5/4}$ and T_R at moderate pressures for polar gases exhibiting hydrogen bonding.

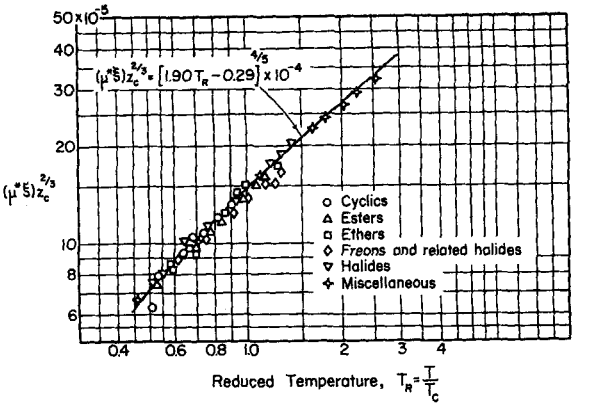

Fig. 2. Relationship between $(\mu^*\xi)z_c^{2/3}$ and T_R at moderate pressures for polar gases not exhibiting hydrogen bonding.

dependent not only on the normalized temperature but also on the reduced dipole energy modulus $\delta^* = \mu^2/2\epsilon\sigma^3$. Besides being complex in application the Krieger potential has been criticized as being unrealistic (2), and the resulting collision integrals have recently been shown to be in error (18).

Monchick and Mason (18) have recently calculated collision integrals for the application of Equation (3) to polar molecules, utilizing a more realistic potential. Collision integrals were calculated for the Stockmayer potential, Equation (5), and were averaged over all possible orientations, assuming that all values of g (ϑ, φ) were equally probable. The resulting collision integrals are again functions of T_N and δ^*. Monchick and Mason conclude that their use of the Stockmayer potential for polar gases gives as good results as the previous use of the Lennard-Jones potential (11) for nonpolar gases. However they indicate that their approach is not applicable to hydrogen bonded substances such as water and ammonia, and it has the disadvantage that it requires both reliable viscosity data for the establishment of the force constants ϵ/κ and σ and a reliable value of the dipole moment before the viscosity values of a polar substance can be calculated.

Because the energy of interaction of hydrogen bonding cannot be expressed in suitable form, and because of the difficulties involved in the application of relationships developed from theoretical considerations for the calculation of the viscosity of polar gases at moderate pressures, a dimensional analysis approach has been advanced in this study to relate the viscosity of a polar substance to other of its physical properties.

DIMENSIONAL ANALYSIS

It is to be expected that the variables influencing the viscosity of polar gases at moderate pressures are the temperature, molecular weight, the critical constants, and the electrical properties of the molecules. If it is assumed that the dipole—dipole interaction is the dominant electrostatic force between the molecules and that the effect of the remaining electrical properties, such as the quadrupole moment and polarizability, is reflected in the critical constants, then the dipole moment may be used as the only variable representing the electrical properties. With this assumption the application of the Rayleigh method of dimensional analysis indicates that the viscosity should depend on the reduced dipole modulus $\mu^2/v_c R T_c$. However since the dipole moment is not truly representative of all the intermolecular forces such as hydrogen bonding, and since the dipole moment is temperature dependent, it would be advantageous to utilize in its place a different variable which is more representative of the true electrostatic nature of the molecules and for which reliable values are readily available.

Bird and Brock (2) indicate that several correlations have recently been attempted in which the critical compressibility factor is utilized in place of the electrical properties of the substance. For example it has been shown (15) that the use of the critical compressibility factor as a third parameter which accounts for molecular interactions has led to excellent P.V.T. correlations for different substances. In view of these considerations z_c was assumed to be an appropriate variable in which all the electrostatic contributions are reflected. When z_c is used as the variable accounting for the electrostatic properties of the molecule, the viscosity becomes only a function of the temperature, molecular weight, and the critical constants of the gas.

The application of the Rayleigh method to these variables is then identical to the development presented previously for the nonpolar gases (36). The resulting relationship is

$$\mu^*\xi = \beta z_c^m T_R^n \qquad (6)$$

where $z_c = P_c v_c/RT_c$ and $\xi = T_c^{1/6}/M^{1/2} P_c^{2/3}$. The group ξ is a characteristic constant for each substance. Therefore the product $\mu^*\xi$ becomes a unique function of both z_c and T_R when experimental evidence is utilized to establish the exponents m and n of Equation (6).

TREATMENT OF VISCOSITY DATA

Reliable experimental data for fifty-three polar gases were used to establish the dependence of the viscosity parameter $\mu^*\xi$ on both z_c and T_R. The substances considered are listed in Table 1 along with their critical temperatures, critical compressibility factors, and calculated values of ξ. The sources of the experimental viscosities used in this work are also listed. A previous study (36) has shown that for nonpolar gases the viscosity parameter $\mu^*\xi$ is independent of z_c. However when the viscosity parameters of the polar gases were plotted vs. reduced temperature, the resulting curves indicated that for these gases $\mu^*\xi$ is dependent on z_c. To determine the exponent of z_c in Equation (6) values of $\mu^*\xi$ were plotted vs. z_c for reduced temperatures $T_R = 0.6$, 0.8, and 1.0. It was observed that the exponent of z_c was the same for all gases which exhibit strong hydrogen bonding, and this exponent was established to be $-5/4$. Similarly it was determined that for all the remaining polar gases the exponent of z_c was approximately $-2/3$.

To establish the dependence of $\mu^*\xi$ on T_R for the gases exhibiting hydrogen bonding, values of $(\mu^*\xi)z_c^{5/4}$ were plotted vs. T_R on log-log coordinates. The single curve which was produced is presented in Figure 1 and can be represented below $T_R = 2.0$ by the following relationship:

$$(\mu^*\xi)z_c^{5/4} = [7.55\,T_R - 0.55] \times 10^{-5} \qquad (7)$$

Although the curve of Figure 1 extends up to $T_R = 3.0$, Equation (7) has been restricted to reduced temperatures of $T_R \leq 2.0$, since at higher temperatures experimental data are available only for water, and the effects of ionization at these high temperatures on the viscosity of these gases are uncertain.

For the other polar gases the product $(\mu^*\xi)z_c^{2/3}$ was plotted vs. reduced temperature and again a single curve, which is presented in Figure 2, resulted. The relationship of Figure 2 can be expressed analytically as

$$(\mu^*\xi)z_c^{2/3} = [1.90\,T_R - 0.29]^{4/5} \times 10^{-4} \quad (8)$$

CONCLUSIONS AND RESULTS

Viscosity values were calculated by means of Equation (7) for the eleven polar substances exhibiting hydrogen bonding and were compared with the corresponding experimental values. For 129 points an average deviation of 1.47% was obtained. The deviations for the individual hydrogen bonding substances are presented in Table 1.

Ordinarily hydrogen chloride is not considered to exhibit a significant hydrogen bonding effect. However its viscosity data were included in this comparison because the viscosity behavior of this substance appears to follow more closely the behavior of the gases exhibiting hydrogen bonding than that of the other polar gases.

Although acetic acid is known to exhibit hydrogen bonding, the viscosity behavior of this substance was found to differ markedly from the behavior of the other gases which exhibit this property. This anomalous behavior results from the chelation of the acetic acid molecules to form cyclic dimers, and therefore acetic acid does not properly belong with compounds whose hydrogen bonding is of a different type. For this reason acetic acid was not included in the comparison of values calculated with Equation (7).

For the forty-one polar gases which do not exhibit hydrogen bonding, viscosity values calculated with Equation (8) for 197 experimental points produced an average deviation of 2.59%. Substances for which the critical constants had to be estimated, and whose viscosity data were of uncertain reliability, were excluded in the comparison if their calculated viscosity values deviated by more than 6%. The average deviation for each substance is presented in Table 1.

For Freons and related halides the calculated viscosity values were in general somewhat lower than the corresponding experimental values. These deviations can be in part explained by the uncertain reliability of the viscosity data and the critical constants for many of these gases. The effect of the strongly electronegative nature of the fluorine atoms might also be responsible for some of these deviations.

TABLE 1. BASIC CONSTANTS, SOURCES OF VISCOSITY DATA, AND AVERAGE DEVIATIONS

	T_c, °K.	z_c	ξ	Average deviation, %	References
Alcohols					
Methanol	513.2	0.220	0.0272	1.82	*7, 41*
Ethanol	516	0.248	0.0264	1.32	*24, 25, 41*
n-Propanol	537	0.251	0.0269	2.19	*23, 41*
i-Propanol	508.8	0.278	0.0258	1.08	*23, 41*
Trimethylcarbinol	508	0.357 (?)	0.0220	3.67	*23*
Amines					
n-Butyl amine	527	0.270	0.0282	5.73	*23*
i-Butyl amine	518	0.278	0.0276	1.02	*23*
Diethyl amine	496	0.267	0.0299	2.84	*23*
Esters					
Ethyl formate	508.5	0.257	0.0252	*	*23*
Propyl formate	538.1	0.259	0.0259	5.24	*23*
i-Butyl formate	540	0.272	0.0267	3.99	*23*
Methyl acetate	506.9	0.254	0.0254	3.73	*23, 25, 41*
Ethyl acetate	523	0.252	0.0268	2.20	*23, 25, 41, 47*
Methyl propionate	519.7	0.270	0.0264	1.25	*23*
Ethyl propionate	536.5	0.270	0.0271	2.40	*23*
Ethers					
Dimethyl ether	400.1	0.287	0.0283	2.83	*21, 40, 46*
Diethyl ether	467	0.261	0.0299	2.52	*7, 21, 24, 25, 37, 40, 47*
Methyl ethyl ether	438	0.267	0.0288	2.36	*21*
Methyl propyl ether	475	0.269	0.0290	1.40	*21*
Methyl isopropyl ether	469	0.275	0.0285	2.09	*21*
Ethyl propyl ether	499	0.270	0.0291	4.55	*21*
Ethyl isopropyl ether	491	0.277	0.0287	1.27	*21*
Dipropyl ether	529	0.296	0.0274	*	*21*
isoPropyl propyl ether	522	0.271	0.0291	5.18	*21*
Di-isopropyl ether	506	0.274	0.0285	*	*21*
Diphenyl ether	764	0.247	0.0235	*	*9*
Freons and related halides					
11 CCl_3F	471.2	0.277	0.0193	4.83	*1*
12 CCl_2F_2	384.7	0.273	0.0211	4.38	*1, 16*
21 $CHCl_2F$	451.7	0.271	0.0198	3.50	*1, 16*
22 $CHClF_2$	369.6	0.263	0.0216	5.13	*1, 16*
113 $C_2Cl_3F_3$	487.3	0.274	0.0196	5.19	*1*
CFH_2Cl	426.7	0.257	0.0228	0.96	*26*
CF_3Cl	543.5	0.157 (?)	0.0243	*	*26*
CFH_2Br	476.7	0.316 (?)	0.0158	3.16	*26*
CF_2HBr	415.9	0.337 (?)	0.0159	2.22	*26*
CF_3Br	340.8	0.368 (?)	0.0159	4.20	*26*
Halides					
Methyl chloride	416.3	0.276	0.0235	2.77	*1, 4, 5, 7, 34, 40, 47*
Methyl bromide	464.0	0.360 (?)	0.0149	*	*26, 40*
Ethyl chloride	460.4	0.274	0.0248	5.71	*7, 47*
Methylene chloride	510	0.277	0.0200	0.36	*4*
Chloroform	536.6	0.293	0.0182	0.92	*4, 25, 37, 41, 47*
Cyclics					
Thiophene	580	0.288	0.0208	0.24	*20*
Methylthiophene	611	0.278	0.0221	1.54	*20*
Pyridine	622	0.259	0.0238	4.78	*20*
Miscellaneous					
Acetaldehyde	461	0.240	0.0291	2.38	*7*
Acetic acid	594.8	0.200	0.0252	*	*19*
Acetonitrile	547.9	0.183	0.0339	2.41	*7*
Acetone	508.7	0.238	0.0286	2.72	*7, 24, 25, 41*
Ammonia	405.5	0.242	0.0284	1.28	*4, 8, 17, 34, 47, 48*
Hydrogen chloride	324.5	0.266	0.0231	1.92	*42*
Hydrogen cyanide	456.7	0.197	0.0378	*	*4*
Sulfur dioxide	430.7	0.269	0.0189	1.38	*34, 35, 40, 43, 44*
Water	647.4	0.231	0.0192	1.34	*3, 4, 10, 13, 28, 29, 30, 31, 32, 33, 38, 39, 45, 47*

* Average deviation greater than 6%; critical constants and reliability of viscosity data uncertain.

Although it has been suggested (22) that hydrogen cyanide exhibits hydrogen bonding, its viscosity behavior does not appear to follow either Equation (7) or Equation (8). Considerable doubt is therefore cast on the reliability of the available viscosity data for this substance, and consequently hydrogen cyanide was not included in either comparison.

For the 197 experimental points which produced an average deviation of 2.59% with Equation (8), values were calculated with both the Bromley-Wilke and Licht-Stechert equations. The Bromley-Wilke equation produced an average deviation of 2.57%, while the Licht-Stechert equation showed an average deviation of 3.62% for these points. Viscosities calculated with Equation (7) were not compared with corresponding values calculated with the Bromley-Wilke and Licht-Stechert equations because their equations do not apply to most gases which exhibit hydrogen bonding.

By the substitution $z_c = P_c v_c / RT_c$ Equation (8) can be expressed as follows:

$$\mu^* = 188.8 \times 10^{-5} \frac{\sqrt{M T_c}}{v_c^{2/3}} [1.90\, T_R - 0.29]^{5/8} \quad (9)$$

In this form Equation (8) shows that the viscosity of nonhydrogen bonded polar gases is dependent on the same variables that define viscosity in the Bromley-Wilke relationship presented in Equation (4). However there is a fundamental difference between Equation (8) and the Licht-Stechert equation, since in the Licht-Stechert equation $\mu^* \xi$ is independent of z_c.

Equations (7) and (8) are analogous to the following equations which have been developed for nonpolar gases (36):

$$\mu^* \xi = 34.0 \times 10^{-5} T_R^{0.94}, \quad \text{for } T_R \leq 1.50 \quad (10)$$

and

$$\mu^* \xi = 17.78 \times 10^{-5} [4.58\, T_R - 1.67]^{5/8}, \quad \text{for } T_R > 1.50 \quad (11)$$

Thus it can be seen that the exponent m of z_c in the product $(\mu^* \xi) z_c^{-m}$ decreases from 5/4 to zero as the electrostatic complexity and the magnitude of the intermolecular forces decrease.

NOTATION

$g(\vartheta,\varphi)$ = angular dependence of the dipole—dipole interaction, $2 \cos \vartheta_a \cos \vartheta_b - \sin \vartheta_a \sin \vartheta_b \cos (\varphi_a - \varphi_b)$

m = exponent, Equation (6)

M = molecular weight

n = exponent, Equation (6)

P_c = critical pressure, atm.

r = intermolecular separation

R = gas constant, 82.055 atm. cc./g.-mole °K.

T = absolute temperature, °K.

T_c = critical temperature, °K.

T_N = normalized temperature, $T/\frac{\epsilon}{\kappa}$

T_R = reduced temperature, T/T_c

v_c = critical volume, cc./g.-mole

z_c = compressibility factor at critical point, $P_c v_c / RT_c$

Greek Letters

β = constant, Equation (6)

δ^* = reduced dipole energy modulus, $\mu^2/2\sigma\epsilon^3$

ϵ = maximum energy of attraction for Lennard-Jones potential, ergs.

ϑ = orientation angle of molecules for Stockmayer potential

κ = Boltzmann constant, 1.3805×10^{-16} ergs./°K.

μ = dipole moment, debyes

μ^* = viscosity at moderate pressure (0.2 to 5 atm.), centipoises

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

σ = collision diameter for Lennard-Jones potential, Å.

φ = orientation angle of molecules for Stockmayer potential

$\Omega^{(2,2)*}(T_N)$ = collision integral for Lennard-Jones potential

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