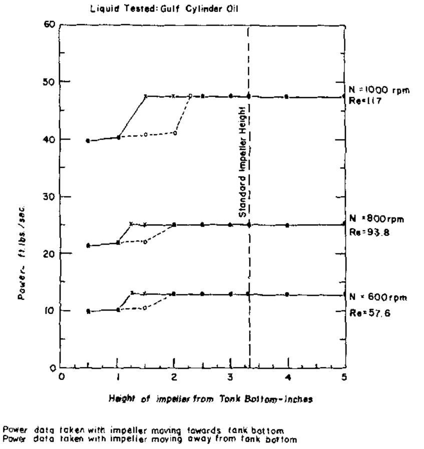

Fig. 1. Experimental hysteresis loop for 10 in. diam. tank.

existed during the upward movement of the impeller. When the impeller is brought sufficiently close to the bottom of the tank, the flow pattern will shift to that of a propeller and the power output will drop. Figure 1 is a typical plot of power output vs. impeller height. The existence of hysteresis, a range of impeller heights in which two power outputs exist, is clearly shown.

If the impeller is stopped and then started, the upper curve in Figure 1 is followed irrespective of the direction in which the impeller is moved. Hysteresis exists only during continuous impeller operation. This effect has been observed at mixing Reynolds numbers of from 20 to 1,000 with the Newtonian materials listed in Table 1. The mixing-power number at the low impeller height is 15% to 20% below the power number for the standard height.

This effect of hysteresis has little practical significance, since the height of an impeller in a tank is rarely, if ever, changed during a process. However, the impeller in a tank is often located near the bottom. The design engineer must take into account the reduced power and altered flow pattern when the impeller is low, so that the equipment is designed to do a satisfactory mixing job. A reduced power output means reduced mixing, and the speed of the impeller should accordingly be increased to compensate.

The Viscosity of Polar Substances in the Dense Gaseous and Liquid Regions

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Jossi, Stiel, and Thodos (*11*) have presented a relationship for the prediction of the viscosity of nonpolar substances. The residual viscosity, $\mu - \mu^*$, was assumed to be a function of the density, molecular weight, and critical constants of the substance, and through a dimensional analysis treatment the correct dependencies were established by the use of experimental data. The resulting relationship, in which the group $(\mu - \mu^*)\xi$ is related to the reduced density, was found to reproduce the reported viscosities for ten substances with a high degree of accuracy. Relationships between $\mu^*\xi$ and T_R, which have also been presented for nonpolar gases (*24*), may be used to calculate the viscosities of these substances at normal pressures (0.2-5 atm.).

Through a dimensional analysis treatment of experimental viscosity data for polar gases, Stiel and Thodos (*25*) have developed the following relationship for polar substances which do not exhibit hydrogen bonding:

$$(\mu^*\xi)z_c^{2/3} = [1.90\,T_R - 0.29]^{4/5} \times 10^{-4} \quad (1)$$

Similarly, they found that for polar gases which exhibit hydrogen bonding

$$(\mu^*\xi)z_c^{5/4} = [7.55\,T_R - 0.55] \times 10^{-5} \quad (2)$$

Values calculated from Equations (1) and (2) were found to compare favorably with the corresponding experimental values.

An approach similar to that used by Jossi et al. (*11*) has been employed to develop a relationship which may be used in conjunction with Equations (1) and (2) for the prediction of the viscosity for polar substances in the dense gaseous and liquid regions. If, as in the previous treatment for the viscosity of polar substances at moderate pressures, the critical compressibility factor, z_c, is considered to be an appropriate variable representing the electrostatic nature of the molecules, the application of dimensional analysis to the residual relationship for viscosity is identical to the previous development for nonpolar substances by Jossi, Stiel, and Thodos (*11*), in which the following expression resulted:

$$(\mu - \mu^*)\xi = \frac{\alpha}{R^{1/6}} z_c^m \rho_R^n \quad (3)$$

TREATMENT OF EXPERIMENTAL VISCOSITY DATA

Experimental high pressure viscosities for the gaseous and liquid phases available in the literature for fourteen polar substances, including five Freons, three alcohols, methyl chloride, chloroform, sulfur dioxide, ethyl ether, ammonia, and hydrazine, were used in conjunction with experimental P-V-T data to establish the constant α and the exponents m and n of Equation (3). The substances are listed in Table 1 along with their critical constants, calculated ξ-values, and the sources of the experimental viscosities and densities utilized.

For each substance values of the quantity $(\mu - \mu^*)\xi$ were calculated from the experimental viscosities and the corresponding values for atmospheric pressure and were plotted against reduced density. Sufficient viscosity data over a complete range of reduced density were available only for methyl alcohol, ethyl alcohol, isopropyl alcohol, ammonia, and ethyl ether. The viscosity data of Golubev and Petrov (*9*), which had not been previously available in this country, were very valuable in establishing the behavior of these substances over a complete range. With the exception of sulfur dioxide only liquid viscosities, many of them for saturated conditions, were available for the other substances.

High pressure density values are not readily available for polar substances, and for several of the substances only viscosity values for saturated conditions could be used because of the lack of density data for other conditions of temperature and pressure. Densities of isopropyl alcohol had to be obtained from the generalized correlation of Lydersen, Greenkorn, and Hougen (*13*) and from the values reported for *n*-propyl alcohol by Ramsay and Young (*18*). The critical density of hydrazine was estimated from the reported saturated liquid densities for the substance (*1*, *29*) by the use of the rectilinear diameter rule proposed by Cailletet and Mathias (*6*).

RESULTS AND CONCLUSIONS

Plots of $(\mu - \mu^*)\xi$ against ρ_R were found to be essentially the same for all

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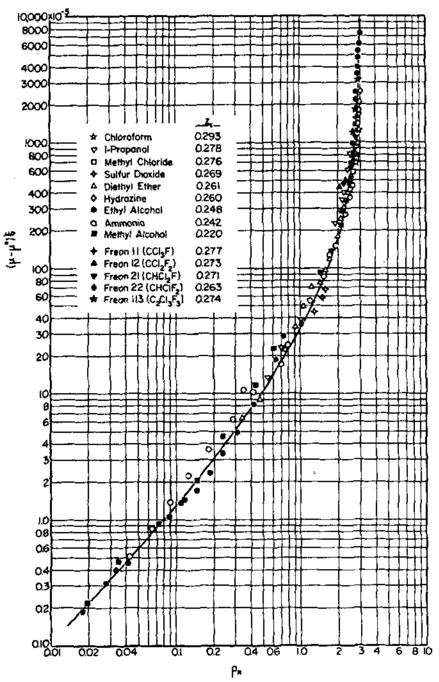

the substances investigated. Therefore, it was concluded that the exponent m of z_c in Equation (3) was zero for polar substances as it was for nonpolar substances. A composite curve relating $(\mu - \mu^*)\xi$ to ρ_R for all the polar substances considered is presented in Figure 1. The viscosity values for the dense gaseous region reported by Shimotake and Thodos (*20*), Stakelbeck (*23*), and Kiyama and Makita (*12*) for ammonia and by Shimotake and Thodos (*21*) and Stakelbeck (*23*) for sulfur dioxide were found to deviate each in a different manner from the unique relationship of Figure 1 and were therefore not included. The viscosity values obtained for ammonia by Golubev and Petrov (9) for the dense gaseous and liquid regions follow the consistent behavior of the other substances. The viscosities determined very recently for ammonia by Carmichael, Reamer, and Sage (7) are consistent with those of Golubev and Petrov (9) at high densities, but deviate from them at lower densities. The correct viscosity behavior of ammonia remains to be verified, but the values of Golubev and Petrov (9) were used in this study because of their agreement with the data for the other substances.

The following analytical representations of Figure 1 were obtained, which permit the rapid calculation of viscosity values:

$$(\mu - \mu^*)\xi = 16.56 \times 10^{-5} \rho_R^{1.111} \qquad \rho_R \leqq 0.10 \qquad (4)$$

$$(\mu - \mu^*)\xi = 0.607 \times 10^{-5} [9.045\rho_R + 0.63]^{1.739} \qquad 0.10 < \rho_R \leqq 0.90 \qquad (5)$$

$$\log \{-\log[(\mu - \mu^*)\xi]\} = 0.6439 - 0.1005\rho_R - \Delta \qquad 0.9 < \rho_R < 2.6 \qquad (6)$$

where

$$\Delta = 0 \text{ for } 0.9 < \rho_R < 2.2$$

and

$$\Delta = 4.75 \times 10^{-4} [\rho_R^3 - 10.65]^2$$

for $2.2 < \rho_R < 2.6$. Values which may be used to calculate the viscosity of a polar substance in the dense gaseous or liquid regions were read from an enlarged plot of Figure 1 and are presented as follows:

ρ_R	$(\mu - \mu^*)\xi$
0.01	0.100×10^{-5}
0.02	0.215
0.04	0.460
0.06	0.720
0.08	1.000
0.10	1.29
0.20	3.00
0.30	5.10
0.40	7.60
0.50	10.5
0.60	13.9
0.70	17.5
0.80	22.0×10^{-5}
0.90	26.5
1.00	32.5
1.2	46.0
1.4	65
1.6	88
1.8	116
2.0	160
2.2	225
2.4	325
2.6	500
2.8	900
3.0	2500

At low densities the values of $(\mu - \mu^*)\xi$ obtained from Figure 1 are slightly lower than the corresponding values resulting from the work of Jossi et al. (*11*) for nonpolar substances; at high densities for the liquid region the curves of the two figures are identical. This is because in liquids the molecules are close together and differences in attractive forces owing to polarity effects become less significant. Reliable viscosity values at low densities are available only for methyl alcohol, ethyl alcohol, isopropyl alcohol, and ammonia, whose z_c values range from 0.220 to 0.278. For these substances the viscosity behavior at low densities appears to be independent of z_c, but additional experimental data are required to verify this conclusion. The effect of the varying polarities of the substances may be accounted for in their viscosity values at atmospheric pressure which were previously found to be dependent on z_c as shown in Equations (1) and (2). For polar gases which do not exhibit hydrogen bonding, these atmospheric viscosities may be calculated from Equation (1); values of μ^* for the polar substances which exhibit hydrogen bonding may be obtained from Equation (2).

TABLE 1. BASIC CONSTANTS AND SOURCES OF VISCOSITY AND P.V.T. DATA FOR POLAR SUBSTANCES

	z_c	T_c, °K	P_c, atm.	ρ_c, g./cc.	ξ	Sources of viscosity data (dense gaseous and liquid phases)	Sources of P.V.T. data (dense gaseous and liquid phases)
Chloroform	0.293	536.6	54	0.50	0.0182	28	28
Methyl chloride	0.276	416.3	65.9	0.353	0.0235	2, 5, 23, 28	28
Sulfur dioxide	0.269	430.7	77.8	0.524	0.0189	2, 21, 23	15
Diethyl ether	0.261	467	35.6	0.264	0.0299	9, 28	4, 26
Freon 11 CCl_3F	0.277	471.2	43.2	0.554	0.0193	5	5
Freon 12 CCl_2F_2	0.273	384.7	39.6	0.555	0.0211	5	5
Freon 21 $CHCl_2F$	0.271	451.7	51.0	0.522	0.0198	5	5
Freon 22 $CHClF_2$	0.263	369.6	48.5	0.525	0.0216	5	5
Freon 113 $C_2Cl_3F_3$	0.274	487.3	33.7	0.576	0.0196	5	5
Methyl alcohol	0.220	513.2	78.5	0.272	0.0272	9, 28	17
Ethyl alcohol	0.248	516	63.0	0.276	0.0264	9, 28	16, 26
i-Propyl alcohol	0.278	508.8	53.0	0.274	0.0258	9	13. 18
Ammonia	0.242	405.5	111.3	0.235	0.0284	8, 9, 12, 20, 23	10
Hydrazine	0.260	653	145	0.334	0.0188	1, 14, 19, 29	1, 14, 19, 29

The experimental high pressure viscosities available for water (*27*) were found to be inconsistent with those of the other polar substances investigated. Jossi, Stiel, and Thodos (*11*) have presented a fourth degree polynomial relationship between $(\mu - \mu^*)\xi$ and ρ_R for this substance. This relationship is higher than that of Figure 1 at low densities and lower at high densities. The reason for the abnormal behavior of water is uncertain, but may be owing to its excessive hydrogen bonding effects. Considerable deviations among the data of the individual investigators have been obtained for this substance (*27*). The relationships developed in this and the previous study (*11*) indicate that the viscosity of both nonpolar and polar substances for high densities in the liquid region (for which μ^* is insignificant compared to μ) is extremely dependent on density. Baschinski (*3*) proposed the following relationship for the viscosity of liquids:

$$\mu = \frac{c}{v - b} \qquad (7)$$

Here c and b are specific constants for each substance, and v is the molar volume. Souders (*22*) has suggested that for organic liquids the quantity log (log μ) is proportional to the density. The relationship of Figure 1 is essentially consistent with such a form at high densities as shown in Equation (6). Experimental data for argon and nitrogen (*30, 31*) indicate that a unique dependence between liquid viscosity and density is exactly correct only at a reduced density of 2.0 and approximately correct at lower reduced densities. At higher reduced densities the relationship between viscosity and density may be quite dependent on temperature. However, in the present study the effects of other variables could not be observed because of the extreme sensitivity of the group $(\mu - \mu^*)\xi$ on ρ_R.

NOTATION

b, c = constants in Equation (7)
m, n = exponents in Equation (3)
M = molecular weight
P_c = critical pressure, atm.
R = gas constant, 82.055 cc. atm./g.-mole °K.
T = temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v = molar volume, cc./g.-mole
v_c = critical volume, cc./g.-mole
z_c = critical compressibility factor, $P_c v_c / RT_c$

Greek Letters

α = proportionality constant in Equation (3)
μ = viscosity, centipoises
μ^* = gaseous viscosity at approximately atmospheric pressure, 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

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Equilibria in the Hydration of Ethylene and of Propylene

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In a previous article by Cope and Dodge (*1*), it was shown that two simultaneous reactions occur when ethylene is hydrated at elevated temperatures and pressure in the presence of a dilute mineral acid as catalyst:

$$C_2H_4 + H_2O = C_2H_5OH \qquad (1)$$

$$2\,C_2H_5OH = C_2H_5OC_2H_5 + H_2O \qquad (2)$$

It was further shown that, while the agreement between directly measured values of equilibrium composition at various temperatures and those calculated from thermochemical data was reasonably good for reaction (1), such was not the case for reaction (2). Based on an analysis of the various thermochemical data then available, it was concluded that the most likely source of the discrepancy lay in the value of the absolute entropy of ethyl

(Continued on page 279)