Viscosity of Ammonia at High Temperature and Pressure

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The viscosity of ammonia on five isotherms in the temperature range 448–598 K and pressures to 121 bar are reported. The measurements were made in a steady-state, capillary flow viscometer. The measurements are estimated to be accurate to better than 0.4% over the full range.

Ammonia is an important chemical of commerce for which reported viscosity measurements do not agree. Ammonia is also a simple, polar gas and a candidate for study by theoreticians seeking to develop theories of the fluid state. This motivated the experimental measurements of the viscosity of ammonia reported here.

Carmichael, Reamer, and Sage (*4*) reviewed the available ammonia viscosity data and presented measurements they made in a rotating cylinder viscometer. Their work did not agree with measurements reported by Kiyama and Makita (*15*) and by Shimotake and Thodos (*21*) in the moderately dense gas regions. All of these measurements were made in the temperature range 370–480 K and pressures below 345 bar. The atmospheric pressure measurements have been reviewed by Groenier and Thodos (*8*) and are not discussed in detail here.

The *P*–*V*–*T* data of ammonia are required to evaluate the viscosity obtained with the steady-flow capillary viscometer in the experiments reported here and to represent the ammonia behavior as a function of gas density. The measurements reported by Beattie and Lawrence (*1*), by Kasarnowsky (*13*), and by Meyers and Jessup (*18*) were used in this study.

The agreement between the ammonia viscosity measurements reported by different investigators is not good. In this study, a series of measurements were made on ammonia in a steady-flow, capillary viscometer at temperatures between 448 and 598 K and pressures to 120 bar. The viscosity data reported by Carmichael et al. (*4*) agree within experimental error on the overlapping isotherms. All other measurements show large deviations at the higher densities.

Experimental Section

The experimental measurements were made in a steady-flow capillary tube apparatus. Details of this experimental system have been presented by Kao, Ruska, and Kobayashi (*12*) and by Flynn, Hanks, Lemaire, and Ross (*6*). Details of the apparatus used in this work at high temperatures are presented elsewhere (*22*) and only the important parts are discussed here.

The Pyrex capillary tube was carefully measured at 298 K and was 305.414 ± 0.0014 mm long and had a mean radius of 0.10323 ± 0.00015 mm. The length was determined with a cathetometer and the mean radius by measuring the mass of a length of mercury thread placed in the capillary tube. These measurements were very carefully done and represent the average of several replications of the measurements.

The capillary tube was placed in a pressure cell with a packing gland to separate the two ends as shown in Figure 1. A thermowell was located in the pressure vessel near the center of the capillary tube and an NBS calibrated platinum resistance thermometer inserted to measure the temperature of each measurement. Two standard high-pressure tube connections were provided on each end of the vessel to measure the pressure and provide gas flow ports at each end of the capillary.

A schematic diagram of the apparatus is shown in Figure 2. Two identical, calibrated piston pumps provided flow of the test gas. These pumps were synchronized to move in opposite directions using a continuous variable speed drive. With this arrangement the test gas volume remained constant during each run. The stroke of these pumps permitted a run 20 min long, much greater than required to obtain the steady-state measurements. Flow rates between 3.6 and 8.5 cm^3/min were used in these measurements.

The pressure of the test gas in the high-pressure cell was measured with high-temperature differential pressure null indicators. Nitrogen gas was used as the pressure transmission fluid. By adjusting the nitrogen pressure to null the differential pressure indicators, the differential pressure across the capillary tube due to the flow of test gas was measured with a mercury U-tube manometer. The U-tube was made of nonmagnetic stainless steel and the meniscus located by floating five steel balls on the mercury surface in each leg of the U-tube. A linear differential transformer was nulled using the steel balls as the transformer core and the differential pressure obtained by measuring the distance between scribe marks on the transformers with a precision cathetometer. The location of the steel ball core center was found to be reproducible to ±0.001 cm. This system yielded differential pressure measurements as accurately as reading a meniscus in a glass tube.

The total pressure was measured with two temperature-compensated dial gauges with 16 in. diameter faces. One gauge was used in the range 0–3000 psia, the other from 0 to 10 000 psia. The total pressure measurements were made when there was no flow through the capillary tube. The differential pressure measurements were made with flow in both directions through the capillary tube to isolate systematic errors in this measurement.

A vacuum pump with an oil diffusion pump was used to evacuate the apparatus before charging the test gas. The system was filled with ammonia and evacuated to ensure that no air or moisture remained in the system.

A constant-temperature bath contained the high-pressure cells with the capillary tube, both differential pressure indicators, and both the piston pumps. Molten salt was used as the bath fluid and the temperature could be controlled to ±0.01 K in the range 423–673 K. The room temperature was controlled at 25.0 ± 0.5 °C to allow the ±0.01 K constant-temperature bath control.

The auxiliary pumps and manifold system to charge the system with ammonia and to adjust the system pressure are described in detail in ref 22.

Warning! Thodos (*23*) has described situations where ammonia in contact with mercury may form compounds that are explosive. This hazard exists when water is present. Mercury was used as a displacement fluid for the ammonia in the experiments described here. Precautions were taken to ensure the system was dry. All transfers were made at room temperature or below. The operating procedure was designed to minimize the time when mercury and ammonia were in contact at high pressure. We recommend that experimenters avoid the use of mercury in contact with ammonia to preclude this hazard.

Capillary Viscometer Equation

The viscosity of a gas can be determined by steady flow through a capillary tube but there are several corrections that must be made to obtain accurate viscosity coefficient data from the experimental measurements. These include the following: (1) the compressibility of the fluid in the capillary tube under the

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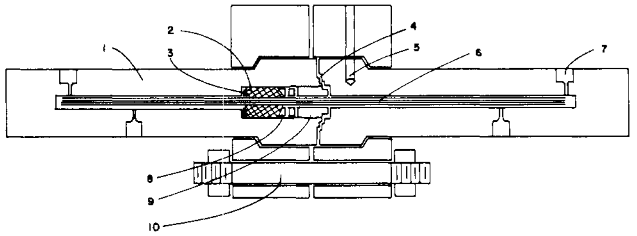

Figure 1. High-pressure cell assembly: 1, pressure cell body; 2, high-temperature packing; 3, packing retaining ring; 4, metal "O" ring seal; 5, thermometer well; 6, capillary tube; 7, high-pressure tubing connection; 8, packing compression ring; 9, packing nut; 10, closure bolt.

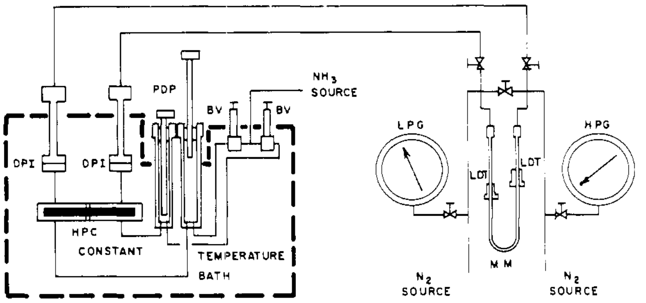

Figure 2. Schematic diagram of the steady-flow capillary viscometer: BV, high-temperature block value; DPI, high-temperature differential pressure null indicators; HPC, high-pressure cell; HPG, high-pressure gauge; LDT, linear differential transformer; LPG, low-pressure gauge; MM, mercury manometer, PDP, positive displacement piston pump.

pressure gradient; (2) the kinetic energy correction of the fluid due to the acceleration of the fluid to fully developed, laminar flow or the Hagenbach correction; (3) the Couette correction due to the contraction and expansion of the fluid as it enters and leaves the capillary tube, this correction was less than 0.05% and was neglected; (4) the change in dimensions of the capillary tube due to the temperature change between the experimental conditions and the temperature at which the capillary tube dimensions were measured; (5) a possible nonuniform diameter over the length of the capillary tube due to the manufacturing technique, careful selection of the capillary tube producing no correction from this source in this work; (6) a possible tangential velocity component at the capillary wall which leads to a slip correction, this correction being proportional to the molecular mean free path length and therefore increasing as the total pressure decreases.

When the corrections for the end effects, the temperature coefficient, and the slip are included, the modified Poiseuille equation becomes

$$\eta = \frac{\pi a^4 \Delta p(1 - \Delta p/2p_1)(1 + 4\xi/a)(1 + \alpha\Delta T)^2}{8Q_e(L + na)} - \frac{[m + \ln(p_1/p_2)]\rho Q_e}{8\pi(L + na)(1 + \alpha\Delta T)} \quad (1)$$

(this equation is not the same form as given in ref 6 but very similar to ref 12).

When the pressure is high, the terms $\Delta p/2p_1$ and $\ln(p_1/p_2)$ both go to zero and eq 1 simplifies to the form

$$\eta = \eta_p - mX \quad (2)$$

where

$$\eta_p = \frac{\pi a^4 \Delta p(1 + 4\xi/a)(1 + \alpha\Delta T)^3}{8Q_e(L + na)} \quad (3)$$

and

$$X = \frac{\rho Q_e}{8\pi(L + na)(1 + \alpha\Delta T)} \quad (4)$$

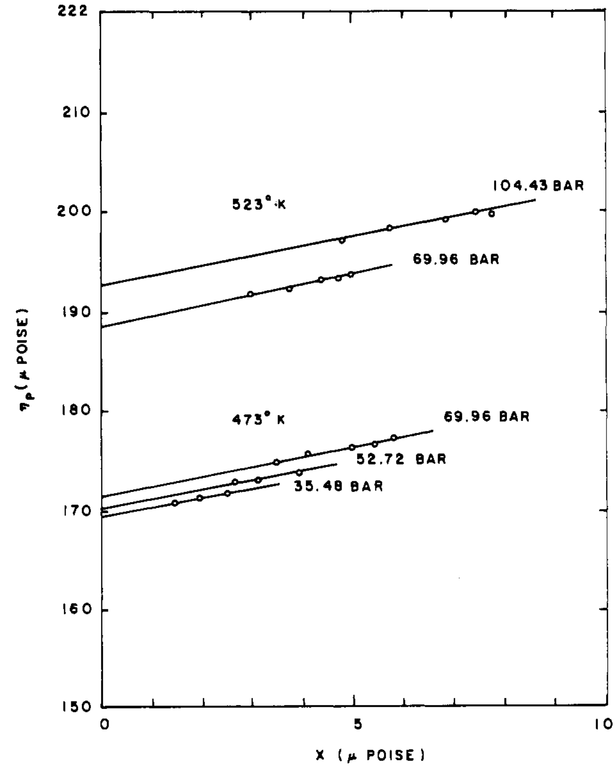

Figure 3. Determination of the Hagenbach factor m. The lines shown have a slope $m = 1.18 \pm 0.01$ determined by measurements on all isotherms.

In this work we assigned $n = 1.2$, an intermediate value determined by Weissberg (*25*) $\alpha = 3.2 \times 10^{-6}$/K, and evaluated the slip coefficient using the expression presented by Knudsen (*16*)

$$\xi = 0.81\left(\frac{8\eta}{3}\right)\left(\frac{2}{\pi p \rho}\right)^{1/2} \quad (5)$$

All of these corrections are small with a total contribution of less than 0.4%, but they are significant in the final results.

The Hagenbach factor (*9*), m, in eq 2 was obtained by computing η_p and X in eq 3 and 4 at several volumetric flow rates at constant temperature and pressure. The viscosity of the fluid must be a constant at the given temperature and pressure so plotting η_p vs. X should produce a line with slope m. Figure 3 shows the results of this procedure at two temperature levels and several pressures. The Hagenbach factor was found to be $m = 1.18 \pm 0.01$ for this instrument.

The ammonia density must be known to evaluate the viscosity in eq 1. Groenier and Thodos (*7*) have reviewed the P-V-T measurements in detail, and from this study, the data from Beattie and Lawrence (*1*), Kasarnowsky (*13*), and Meyers and Jessup (*18*) were used to obtain constants for the Benedict-Webb-Rubin equation of state for ammonia. The B-W-R constants were obtained using a computer program written by Dripps (*5*) to represent 137 data points in the range $422 < T < 598$ K and pressures to 260 bar with a standard error of estimate of 0.1%.

Results

The viscosity of ammonia was measured on five isotherms (448.15, 473.15, 523.15, 573.15, and 598.15 K) and pressures up to 121.6 bar. At each temperature and pressure, Δp was measured across the capillary for several flow rates, Q_e, and the values of η_p and X were computed in eq 3 and 4. These experimental points provided the Hagenbach correction factor and the value of $\eta(T,P)$ when $X = 0$ in eq 2. The Reynolds number for all of the experimental points was less than 1800.

Table I. Viscosity of Ammonia (μP)

pressure, bar	temperature, K				
	448.15	473.15	523.15	573.15	598.15
a	158.48	168.25	187.42	205.87	215.46
6.525	158.49	168.55			
12.047	158.49	168.77	187.47	205.83	215.49
18.248	158.50	168.98	187.48	205.84	215.52
35.484	158.75	169.40	187.53	206.13	215.72
52.719	158.89	169.90	187.75	206.80	216.10
69.964	162.95	170.79	188.39	207.79	216.68
104.435		176.44	192.24	210.49	218.56
121.670		182.28	196.38	212.05	219.94

[a] Values obtained by extrapolation to zero pressure.

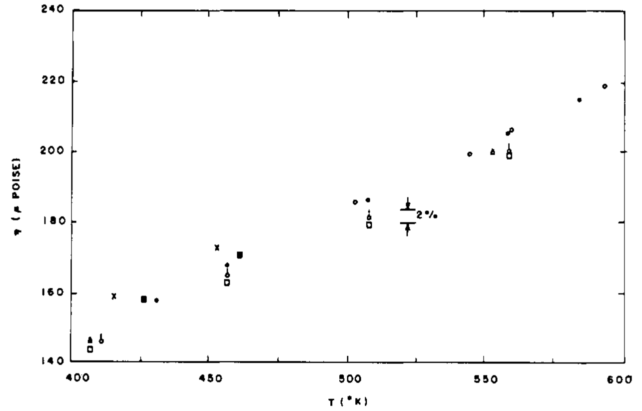

Figure 4. Viscosity of ammonia at low pressure: O, Braune, Link (*2*); Δ, Trautz, Heberling (*24*); □, Kiyama, Makita (*15*); ■, Carmichael, Reamer, Sage (*4*); X, Pal, Barua (*19*, *20*); ȯ, Burch, Raw (*3*); ●, this work.

It is important that the flow be laminar in these experiments (*6*).

The smoothed viscosity data are listed in Table I. The accuracy of these data is better than 0.4% based on an analysis of the assignable errors and upon the reproducibility of the individual experimental points.

The low-pressure measurements reported here are compared with data presented by Braune and Link (*2*) and by Carmichael et al. (*4*) in Figure 4. The agreement is within 1% where the measurements overlap. Another set of these measurements by Trautz and Heberling (*24*), Kiyama and Makita (*15*), and Burch and Raw (*3*) also agrees within 1% but deviates by 3 or 4% from the first set. In a critical assessment of viscosity data, Maitland and Smith (*17*) have shown that viscosity measurements reported by Trautz and co-workers on many gases show systematic deviations from other measurements that become larger as the temperature increases. Kiyama and Makita and Burch and Raw used data from Trautz to calibrate their instruments and therefore their measurements show the same deviations as Trautz's measurements.

There are three sources of high density ammonia viscosity data reported. These data are compared in Figure 5. The agreement between measurements by Carmichael et al. (*4*) and this work is within the accuracy of the two measurements. At low temperature, the Carmichael et al. measurements agree well with ammonia viscosity measurements reported by Iwasaka, Kestin, and Nagashima (*10*). The former measurements were made with a rotating cylinder instrument; the latter, with an oscillating disk instrument. Agreement between these measurements and those reported here suggests that in the regions of overlapping fluid states, these instruments provide the same values for the ammonia viscosity.

Shimotake and Thodos (*21*) measured the ammonia viscosity on the 473 K isotherm using a nonsteady flow capillary viscometer. Their measurements show a much stronger density dependence with a value nearly the same as that of Carmichael et al. and this work at zero density.

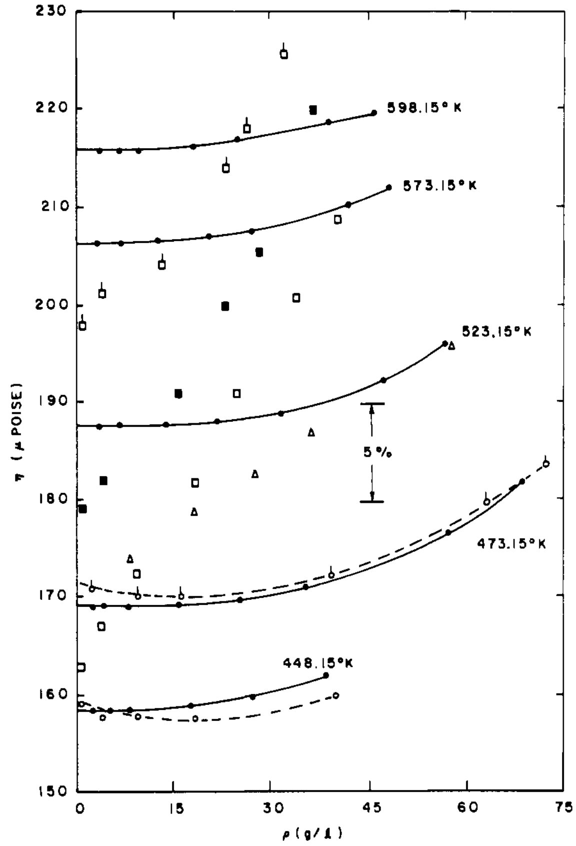

Figure 5. Viscosity of ammonia as a function of density: Carmichael, Reamer, Sage (*4*), (O) 444.15 K, (ȯ) 477.15; Kiyama, Mikila (*15*), (□) 473.15 K, (◫) 523.15 K, (⊡) 573.15 K; Simotake, Thodos (*21*), (Δ) 473.15 K; this work, (●).

Kiyama and Makita (*15*) report three isotherms at 473, 523, and 573 K. Their measurements were made using a rolling ball viscometer and show an even stronger density dependence. We are unable to explain the differences between these measurements and our data. Correcting the Kiyama and Makita measurements for the calibration error introduced by using Trautz's data for calibration only increases the differences at high density.

We note that Carmichael et al. measured an initial decrease in viscosity with increasing ammonia density on the 448 and 473 K isotherms. A decrease in viscosity with density was not observed in this work. Iwasaki, Kestin and Nagashima (*10*) have reported this negative viscosity dependence at low pressure on the 293 and 303 K isotherms. Iwasaki and Takahaski (*11*) noted that this negative dependence decreases as the temperature increases and was not observed above 410 K or at temperatures above the vapor-liquid critical point. All of the measurements reported here are above 410 K.

Inspection of Figure 4 shows that the viscosity-density isotherms for ammonia are nearly parallel. This suggests that a residual correlation of the form

$$\Delta\eta(\rho) = \eta(T,\rho) - \eta_0(T,\rho = 0)$$

could represent the effect of density on the ammonia viscosity. A least-squares fit of a third degree polynomial

$$\Delta\eta = 0.07387 + 0.0015\rho + 0.00117\rho^2 + 0.0003\rho^3$$

where ρ is the density in grams per liter represents the ammonia data in Table I within experimental error.

Conclusions

The ammonia viscosity data presented here have extended the range of these data to 598 K and pressures to 121 bar.

These data are consistent with the measurements of Carmichael et al. (*4*) on the two isotherms where the measurements are reported at nearly the same temperature. The negative slope of the ammonia viscosity with density observed at low temperature and reported by Carmichael et al. at about 473 K was not observed in these measurements. This effect is small and very careful experiments must be done to observe it.

Glossary

a	capillary tube radius
L	length of the capillary tube
m	Hagenbach factor
n	Couette factor
p_1	pressure at inlet of the capillary tube
p_2	pressure at outlet of the capillary tube
Δp	$p_1 - p_2$, pressure drop across the capillary tube
Q_e	volumetric flow rate at the inlet of the capillary tube
T	temperature
ΔT	temperature at experimental conditions minus $T =$ 298.15 K
X	term defined by eq 4

Greek Symbols

α	linear thermal expansion coefficient for the capillary tube material
η_0	viscosity at low density
η_p	Poiseuille's law viscosity defined by eq 3
ξ	viscous slip coefficient
ρ	gas density

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Vapor Pressure of 3,4-Diethyl-3,4-hexanediol

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The vapor pressure of 3,4-diethyl-3,4-hexanediol was determined for a wide range of temperatures. The temperature dependence of the vapor pressure was expressed by an Antoine equation of the form ln P/torr = −4215.352/(189.301 + t/°C) + 16.5993.

The literature dealing with the vapor pressures of organic compounds is extensive (*1–6*). However, for the larger diols, there is very little information available. The only literature source (*7*) for the 3,4-diethyl-3,4-hexanediol provides insufficient, unreliable information. To deal with some hydrogen bonding problems, we needed accurate vapor pressure data for the 3,4-diethyl-3,4-hexanediol in a wider temperature range than was available and so we determined it experimentally.

Experimental Section

The 3,4-diethyl-3,4-hexanediol was synthesized in our laboratory by a pinacol reaction of 3-pentanone with magnesium in a solvent. The product was purified repeatedly by vacuum distillation and crystallization until gas chromatographic analysis failed to show any significant impurities. The small difference between the boiling point and condensation temperatures, 0.003 °C, measured in a differential ebulliometer (*8*, *9*) at a pressure of 10 torr, indicated that the sample did not contain sufficient impurities of different volatility to have any significant effect on the vapor pressure measurement. The physical constants of the pure substances were found to be the following: $d_4^{25} =$ 0.94350 g cm^{-3}, normal boiling point 233.7 °C, and freezing point 25–26 °C.

The vapor pressures were measured by a dynamic method using two ebulliometers connected in parallel to a pressure controlling system (*4*). One of the ebulliometers contained deionized, twice distilled water and the other was filled with the organic substance. From the boiling point of water, the corresponding pressure in the system was determined with an accuracy of better than 0.1 torr. The boiling points of water and the organic substance, respectively, were measured simultaneously with two 25-Ω platinum resistance thermometers in a Mueller bridge circuit (Leeds and Northrup) with an accuracy of better than 0.01 °C for water but only ±0.03 °C for the diol. The temperature of the water remained constant during the measurement while the temperature of the diol (a very viscous liquid) fluctuated within ±0.03 °C under the same conditions. Since the resistance thermometers were fully immersed in both liquids, it is our opinion that the fluctuation was caused by small temperature differences in the boiling diol due to its poor heat conductance. Both thermometers had been recently calibrated by the National Bureau of Standards.

Results and Discussion

The experimental data listed in Table I were fitted by the least-squares method to an Antoine equation of the form

$$\ln P/\text{torr} = -\frac{4215.352}{189.301 + t/{}^\circ\text{C}} + 16.5993$$