Viscosity of Ammonia at High Pressures

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The viscosity of ammonia in the liquid and gas phases was measured at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 400° F. The measurements were obtained with a rotating-cylinder viscometer, and results are presented in tabular and graphical form. Comparison with earlier measurements indicated fair agreement. The viscosity excess appeared to be a single-valued function of the specific weight.

FROM AN INDUSTRIAL standpoint, a knowledge of the viscosity of fluids is valuable both for equipment design and process control. Investigations of the viscosity of ammonia have been made along the bubble-point curve by Pinevich (*10*), Shatenshtein (*14*), and Stakelbeck (*17*), while Kiyama and Makita (*8*) have studied the gas-phase and Shimotake (*15, 16*) the dense-phase regions. Carmichael (*2*) more recently reported investigations of the liquid phase. These latter measurements were carried out with a rolling-ball viscometer. Shimotake (*15, 16*) measured the viscosity of ammonia at pressures up to 5000 p.s.i.a. at temperatures between 212° and 392° F. The numerous experimental measurements at atmospheric pressure, which have been reviewed by Groenier and Thodos (*4*), will not be considered here. The volumetric behavior of ammonia has been studied by Keyes (*6*) and reported by the National Bureau of Standards (*9*). These latter data are needed to depict the behavior of transport properties with specific volume.

The agreement among the several investigators who have studied the viscosity of ammonia at elevated pressures is not good (*4*) and, therefore, an investigation supplemental to that carried out by Carmichael (*2*) was undertaken to determine the viscosity of ammonia in the gaseous and liquid phases at pressures from atmospheric to 5000 p.s.i.a. in the temperature interval between 40° and 400° F. These measurements were carried out with a rotating-cylinder viscometer (*11*).

EQUIPMENT

The equipment used in this investigation has been described in some detail (*11*), and the methods for evaluating the viscosities indicated by the rotating-cylinder viscometer have also been set forth (*3*). In principle, the instrument consists of a rotating cylinder driven at a predetermined angular velocity. A stator mounted upon a small suspension is hung within the rotating cylinder. The drag of the fluid in the annular space between the stator and the cylinder causes an angular rotation of the stator which is measured. The rotating cylinder and the stator are mounted within a pressure vessel with appropriate transducer equipment to establish the angular displacement within 1 or 2 seconds of arc, and the speed of rotation of the cylinder within 0.05%. The temperatures were measured with a strain-free, platinum-resistance thermometer with an uncertainty of not more than 0.05° F. relative to the international platinum scale. Pressures were determined with a balance (*13*) which had been calibrated against the vapor pressure of carbon dioxide at the ice point (*1*). These pressures were known within 0.1 p.s.i. or 0.5%, whichever is the larger measure of uncertainty.

To ascertain that the behavior of the rotating-cylinder viscometer did not undergo change during the investigation, the viscosity of helium was periodically determined at substantially atmospheric pressure. These values for the viscosity of helium, as established from the torsional elastic properties of the suspension and the dimensions of the stator and rotating cylinder, agreed within 1.8% with the critically chosen values of Hilsenrath (*5*).

During the investigation the only change experienced in the characteristics of the rotating-cylinder viscometer was a small increase in the torsional elastic constant of the suspension. This change apparently resulted from the slight work-hardening of the suspension. The elastic behavior of the suspension was ascertained at each temperature by determining the frequency of oscillation of the stator when the external cylinder was not rotating. Variation in the elastic constant of the suspension with temperatures, as determined from the frequency of the rotor, agreed within 0.1% with the variation in the elastic modulus of the material used in the suspension, as described by Rode (*12*). The suspension was 0.0065 inch in diameter and was constructed of an alloy containing 0.90 weight fraction platinum. The behavior of the instrument could be related to dimensions of the viscometer and the elastic behavior of the suspension (*3*) as shown in

$$\eta_{T,P} = \frac{\phi}{S}[f_1(T,P)][f_2(T,\theta)] = \frac{\phi}{S}k_1k_2 \qquad (1)$$

The second equality in Equation 1 indicated that all the dimensions may be combined in a single factor k_1, which is a function of temperature and presssure. Variation in the elastic behavior of the suspension with temperature and time was taken into account by the second factor k_2.

In the upper part of Figure 1, the value of the configuration factor, k_1, is shown as a function of temperature for two pressures. The suspension factor, k_2, which is depicted in the lower part of Figure 1, shows the change in the elastic behavior of the suspension with time. The values of k_1 are determined entirely from measurements of the dimensions of the stator and rotor and of the predicted effect of temperature and pressure upon these dimensions. In addition, the variation in the elastic behavior of the suspension with respect to temperature and time has been included in the factor k_2. The factor k_2 was established experimentally from the variation in the elastic behavior of the suspension with respect to temperature and time.

MATERIALS

The helium obtained from Air Reduction Pacific Co. was reported and confirmed by mass spectrographic analysis to contain less than 0.003 mole fraction material other than helium. The ammonia was obtained from the

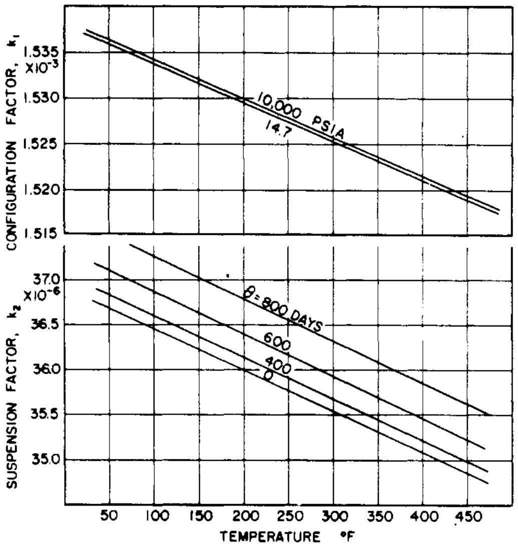

Figure 1. Effect of temperature and pressure on behavior of viscometer

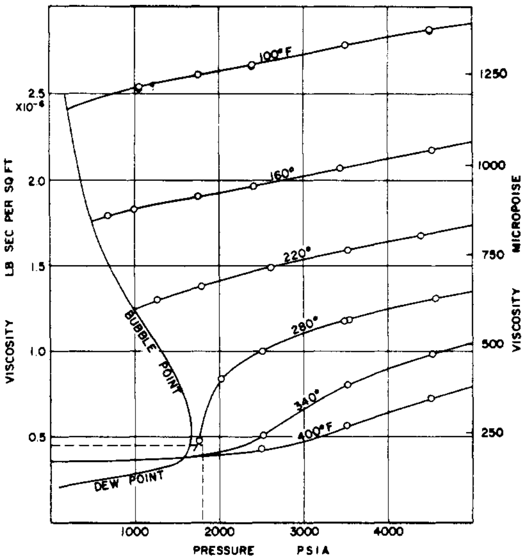

Figure 2. Effect of pressure on viscosity of ammonia.

Matheson Co. who reported it contained less than 0.001 mole fraction material other than ammonia. Spectrographic analysis indicated it contained 0.0007 mole fraction nitrogen and 0.0031 mole fraction hydrogen. After passing over anhydrous calcium sulfate, the ammonia was condensed and evacuated for an extended period at liquid nitrogen temperature to remove a portion of the small quantities of nitrogen and hydrogen which were indicated to be present by the spectrographic analysis.

RESULTS

The effect of pressure upon the viscosity of ammonia is portrayed in Figure 2 for the temperatures investigated. Experimental points have been included at the higher pressures. To permit behavior at the lower pressures to be more fully portrayed, this region has been presented separately in Figure 3 where the experimental points are included. Values obtained for the viscosity of ammonia for both the gas and liquid phases are recorded in Table I. The values are tabulated in micropoises because of the apparently widespread use of this unit even in engineering work. However, the results are presented in the figures in terms of pounds second per square feet and in micropoises. These data were obtained over a period of approximately six months and many check measurements were made to ascertain that no gradual shift in the behavior of the rotating-cylinder viscometer influenced the results. The curves shown in Figures 2 and 3 have been smoothed with respect to temperature and pressure. Table II records smooth values of the viscosity of ammonia for a series of temperatures and pressures. The standard error of estimate of the smooth values from the experimental data was 0.003×10^{-6} pound second per square foot, or 14 micropoises. These data involved 97 experimental points at specific weights below the critical state. At specific weights greater than that at the critical state, with 79 experimental points involved, data yielded a standard error of estimate of 0.007×10^{-6} pound second per square foot or 34 micropoises. These standard errors of estimate correspond to 0.34% relative to a mean viscosity of 1.46×10^{-6} pounds second per square foot.

Comparison of the data of several investigators for ammonia in liquid phase at bubble point is portrayed as a function of temperature in Figure 4. As indicated in the earlier work of Carmichael (*2*), there is significant deviation between the experimental measurements of Pinevich (*10*) and Shatenshtein (*14*). Fair agreement between the measurements of Carmichael (*2*) at bubble point and the present study was obtained. However, Carmichael's data showed a much more rapid decrease in viscosity at bubble point with increase in temperature than was found in the present measurements. This may well be due to the difficulties in properly evaluating the effect of turbulence upon the behavior of the rolling-ball viscometer used by Carmichael. The present instrument does not suffer from such effects to any measurable extent.

Deviation of measurements in the gas phase by Kiyama and Makita (*8*), Stakelbeck (*17*) and Shimotake (*15, 16*) from the present data is set forth in Figure 5 as a function of pressure for the several temperatures studied by these investigators. To permit a direct comparison with the experimental measurements reported by other investigators it was necessary to interpolate the present values to the temperatures involved in the several investigations. The measurements of Stakelbeck (*17*) indicate a smaller change in viscosity with temperature and a large change with pressure than the present measurements. The disagreement at pressures of approximately 300 p.s.i.a. and at a temperature of 176° F. is nearly 40%. Rather satisfactory agreement with the measurements of Kiyama and Makita (*8*) in the temperature interval between 122° and 302° F. was realized at pressures up to about 600 p.s.i.a. At higher pressures the data of Kiyama and Makita indicated a more rapid increase in viscosity with pressure than was found in the present measurements.

In the liquid phase the current measurements are about 7% below the values reported for Carmichael (*2*) at 100° F. As was shown in Figure 4 somewhat better agreement was realized at 130° F. and at 160° F. The data of Carmichael indicate a more rapid decrease in viscosity with an increase in temperature than the present measurements and a slightly smaller change in viscosity with pressure. In the lower part of Figure 5 a comparison is made with the measurements of Shimotake (*15, 16*) in the temperature interval between 212° and 392° F. At pressures below 2000 p.s.i.a. fair agreement was realized. However, at the higher pressures the data of Shimotake (*15, 16*) show a smaller effect of pressure upon the viscosity of ammonia than the present measurements. For reasons that are not entirely clear the available viscosity data for ammonia disagree to a much larger extent than measurements for such fluids as ethane (*3*). The present data provide hitherto unavailable measurements made with a rotating-cylinder

Table I. Experimental Measurements for Ammonia

Pressure, P.S.I.A.	Viscosity, Lb. Sec./Sq. Ft.	Viscosity, Micropoise
	100° F.	
	$\times 10^{-6}$	
5349.2	2.93731	1406.35
5262.3	2.93406	1404.80
5262.3	2.92834	1402.06
4506.7	2.85789	1368.33
4506.7	2.86015	1369.41
3508.6	2.77231	1327.35
3508.6	2.77194	1327.18
2829.0	2.70830	1296.71
2401.4	2.65959	1273.38
2393.2	2.66156	1274.33
1749.8	2.60697	1248.19
1746.2	2.60857	1248.96
1029.0	2.53716	1214.77
1027.1	2.52737	1210.08
383.3	2.44404	1170.18
382.9	2.44700	1171.60
173.0	0.21807	104.41
172.3	0.21788	104.32
171.6	0.21742	104.10
17.0	0.22236	106.46
17.0	0.22236	106.46
17.0	0.22284	106.69
	160° F.	
	$\times 10^{-6}$	
5665.6	2.26131	1082.69
5656.3	2.25653	1080.40
4533.6	2.17294	1040.38
4522.2	2.17221	1040.03
3441.6	2.07319	992.62
3428.3	2.07028	991.23
2413.3	1.96892	942.70
2405.0	1.97634	946.25
1747.0	1.90632	912.73
1746.2	1.91011	914.54
1029.3	1.83469	878.43
1029.3	1.83382	878.01
691.4	1.79302	858.48
686.0	1.79413	859.01
175.5	0.24678	118.16
175.1	0.24660	118.07
173.9	0.24714	118.33
25.9	0.24802	118.75
25.9	0.24821	118.84
25.9	0.24861	119.03
	220° F.	
	$\times 10^{-6}$	
5410.5	1.76178	843.52
5404.3	1.75905	842.21
5400.1	1.76250	843.87
4398.2	1.67398	801.48
4394.1	1.67713	802.99
3526.5	1.59853	765.36
3519.9	1.59261	762.53
2612.7	1.48806	712.47
2612.7	1.48775	712.32
1779.1	1.38360	662.45
1779.2	1.38462	662.94
1266.5	1.30365	624.17
1265.4	1.30163	623.21
899.9	0.28410	136.02
899.9	0.28613	137.00
899.9	0.28579	136.83
899.9	0.28809	137.93
848.9	0.28133	134.70
848.9	0.28202	135.03
800.2	0.28095	134.52
800.2	0.28323	135.61
800.2	0.28310	135.55
800.2	0.27922	133.69
800.2	0.28039	134.25
800.2	0.28416	136.05
609.3	0.27404	131.21
609.3	0.27597	132.13
609.3	0.27522	131.77
609.3	0.27382	131.10
609.3	0.27543	131.98
609.3	0.27570	132.00
498.3	0.27449	131.42
498.3	0.27435	131.36
410.3	0.27381	131.10
410.3	0.27192	130.19
410.3	0.27525	131.79
410.3	0.27479	131.57
213.6	0.27262	130.53
213.6	0.27100	129.75
213.6	0.27311	130.76
213.6	0.27271	130.57
173.0	0.27503	131.68
171.1	0.27533	131.83
170.5	0.27590	132.10
17.0	0.27763	132.93
17.0	0.27866	133.42
17.0	0.27692	132.59
16.8	0.27533	131.83
16.8	0.27436	131.36
16.8	0.27303	130.72
16.8	0.27105	129.78
15.8	0.27514	131.73
15.8	0.27486	131.60
15.8	0.27345	130.93
15.8	0.27443	131.39
	280° F.	
	$\times 10^{-6}$	
5740.5	1.42614	682.82
5740.5	1.42416	681.87
5740.5	1.42524	682.39
4567.6	1.30871	626.60
4567.6	1.30829	626.40
4567.6	1.30702	625.79
3535.4	1.18138	565.63
3535.4	1.18274	566.28
3489.9	1.17798	564.00
2511.4	0.99134	474.64
2511.4	1.00644	481.87
2511.4	1.00632	481.82
2019.9	0.84138	402.84
2019.9	0.83979	402.08
2019.9	0.83940	401.90
1760.4	0.47581	227.81
1760.4	0.47816	228.94
1760.4	0.47706	228.41
1503.3	0.35077	167.95
1503.3	0.35091	168.01
1247.3	0.32582	156.00
1247.3	0.32412	155.19
1247.3	0.32423	155.24
599.4	0.30275	144.95
598.9	0.30312	145.13
598.9	0.30308	145.11
599.4	0.30275	144.95
205.2	0.30063	143.94
205.2	0.30005	143.66
171.6	0.30282	144.99
171.6	0.30302	145.08
171.1	0.30482	145.94
20.7	0.29991	143.59
20.7	0.29977	143.53
18.4	0.30539	146.22
18.4	0.30601	146.51
18.4	0.30679	146.89
	340° F.	
	$\times 10^{-6}$	
5680.0	1.11902	535.78
5680.0	1.12024	536.36
5680.0	1.12556	538.91
4529.5	0.98670	472.42
4529.5	0.98710	472.61
3519.6	0.80432	385.10
3519.6	0.80366	384.78
2522.5	0.50589	242.21
2522.5	0.50607	242.30
1480.5	0.36098	172.83
1480.5	0.36096	172.82
989.1	0.34015	162.86
989.1	0.34061	163.08
405.6	0.33031	158.15
405.6	0.33037	158.18
205.8	0.32923	157.63
205.8	0.32898	157.51
175.2	0.33403	159.93
175.2	0.33320	159.53
175.0	0.33340	159.63
25.7	0.33694	161.32
25.7	0.33804	161.85
18.3	0.33323	159.55
18.3	0.33368	159.76
18.3	0.33329	159.58
	400° F.	
	$\times 10^{-6}$	
5914.9	0.90549	433.54
5914.9	0.90551	433.55
5907.9	0.90288	432.29
4514.2	0.72838	348.74
4514.2	0.72904	349.06
3555.6	0.56894	272.40
3555.6	0.56833	272.11
2499.7	0.43220	206.93
2499.7	0.43137	206.54
1501.3	0.37539	179.73
1501.3	0.37540	179.74
990.2	0.36170	173.18
990.7	0.36270	173.66
397.8	0.35406	169.52
397.8	0.35302	169.02
206.0	0.35480	169.87
207.2	0.35051	167.82
30.3	0.35656	170.72

viscometer. Until good agreement between measurements carried out with markedly different types of instruments is realized, reported values of viscosity must be considered tentative.

The effect of temperature upon the viscosity of ammonia in both the gas and liquid phases is shown in Figure 6. It is to be expected that with an increase in temperature the viscosity of the gas phase will increase progressively. Conversely, the viscosity of the liquid phase decreases rapidly with an increase in temperature.

It has often been assumed that the viscosity excess, which is the difference between the viscosity at attenuation and

Table II. Viscosity of Ammonia in the Liquid and Gas Phases

Pressure, P.S.I.A.	Temperature, ° F.					
	100	160	220	280	340	400
	(212)[a]	(494)	(987)			
Dew Point	104.4	117.3	136.9			
Bubble Point	1155.8	842.7	595.6			
14.7	106.53[b]	119.60	132.72	145.70	158.72	171.65
200	104.62	117.69	130.81	143.83	156.95	169.68
400	1171.98	116.82	130.14	143.49	156.80	169.73
600	1186.20	852.25	131.19	144.26	157.47	170.45
800	1199.61	865.56	133.58	146.37	158.96	171.65
1000	1211.05	876.95	597.53	149.53	161.59	173.56
1500	1236.62	901.18	641.96	168.82	173.80	179.55
2000	1259.79	924.06	678.11	390.69	197.26	189.12
2500	1280.95	947.62	709.57	478.89	239.63	200.61
3000	1301.35	971.08	736.14	528.58	316.96	224.65
3500	1321.70	994.92	761.75	565.07	382.31	263.57
4000	1343.29	1017.04	785.21	596.67	432.83	307.14
4500	1366.23	1039.69	809.39	623.48	468.64	347.36
5000	1390.40	1061.96	831.66	646.37	499.86	378.96
σ[c]	2.25	4.50	1.29	2.11	1.68	2.82

[a] Values in parentheses represent vapor pressures expressed in p.s.i.
[b] Viscosity expressed in micropoise.
[c] Standard error of estimate expressed in micropoise: $\sigma = \left[\left\{\sum_{1}^{N} (\eta_e - \eta_s)^2\right\}/N\right]^{1/2}$

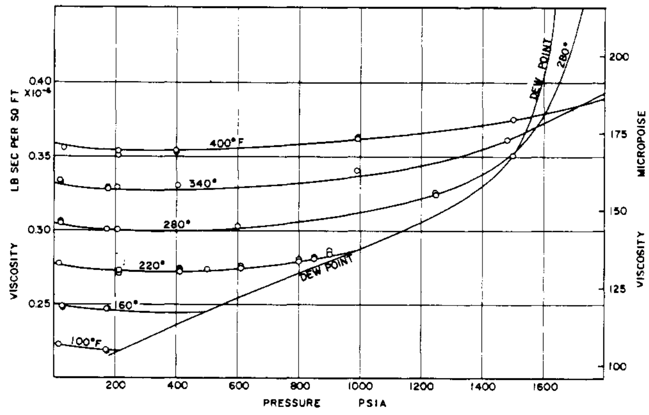

Figure 3. Viscosity of ammonia in the gas phase at low pressures

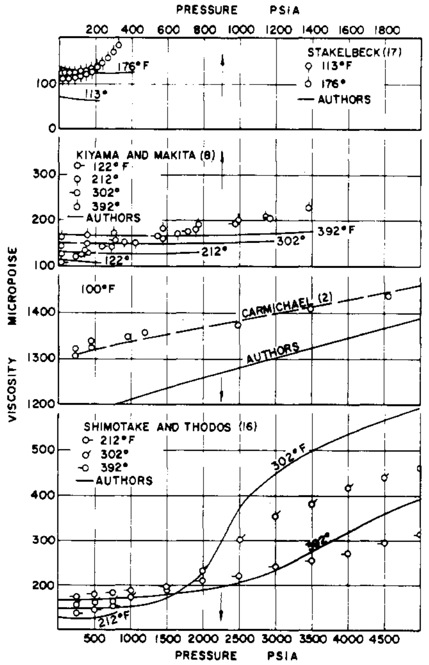

Figure 5. Deviation of measurements at elevated pressures from several investigators

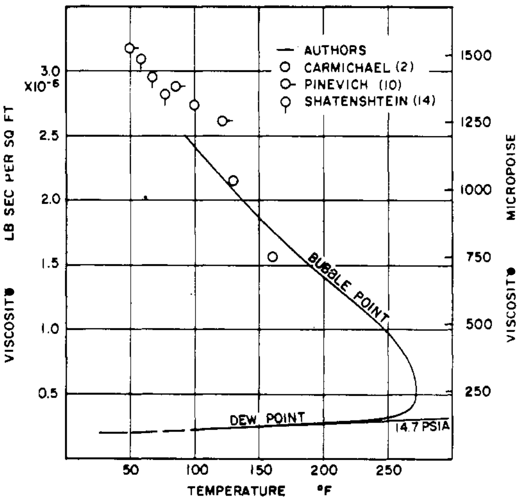

Figure 4. Comparison of viscosity of ammonia at atmospheric pressure and at bubble point from measurements of several investigators

the pressure in question, is a single-valued function of the specific weight. Shown in Figure 7 is the viscosity excess as a function of the specific weight of ammonia for both the gas and liquid phases. The values of viscosity at attenuation ($P = 0$) are smooth values predicted from measurements near atmospheric pressure. A single simple curve has been drawn through these data, and the standard error of estimate of all the points shown from this single curve was 0.011×10^{-6} pound second per square foot or 53 micropoises. In the absence of satisfactory volumetric data at the higher temperatures, points for 340° and 400° F. have not been shown. The behavior at the lower pressures in the gas phase has been presented in a separate part of Figure 7. It should be emphasized that the scale used for the insert is very much larger than that for the main body of the figure. At these low pressures the standard error of estimate of all the experimental data in the gas phase from the single curve drawn through the data was 0.002×10^{-6} or 10 micropoises.

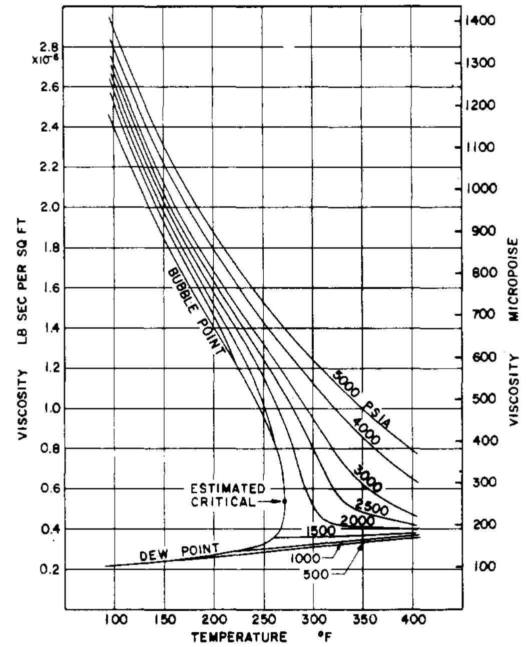

Figure 6. Effect of temperature on viscosity of ammonia

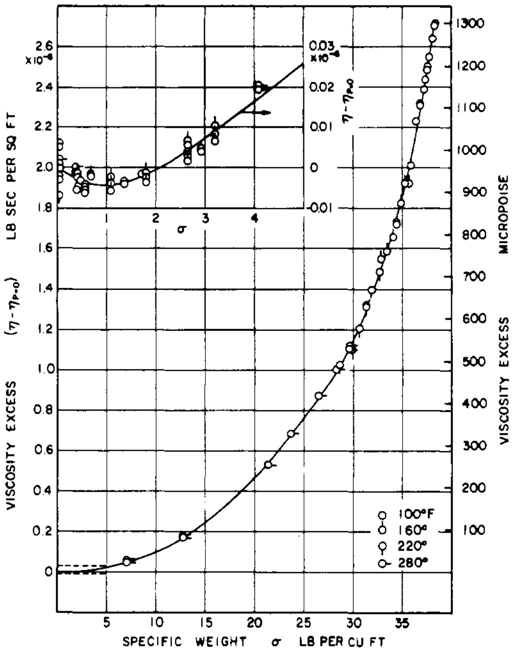

Figure 7. Viscosity excess of ammonia

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NOMENCLATURE

f_1, f_2 = specific functions
k_1 = configuration factor, 1/cu. ft.
k_2 = suspension factor, ft. lb./radian
N = number of experimental points
P = pressure, p.s.i.a.
S = speed of rotation, rev./sec.
T = absolute temperature, ° R.
η = viscosity, lb. sec./sq. ft. or poise
θ = time, sec.
σ = specific weight, lb./cu. ft.
σ = standard error of estimate
ϕ = angular displacement, degrees of radian

Subscripts

e = experimental
P = pressure
s = smooth
T = temperature

LITERATURE CITED

(1) Bridgeman, O.C., *J. Am. Chem. Soc.* **49**, 1174 (1927).
(2) Carmichael, L.T., Sage, B.H., *Ind. Eng. Chem.* **44**, 2728 (1952).
(3) Carmichael, L.T., Sage, B.H., J. CHEM. ENG. DATA **8**, 94 (1963).
(4) Groenier, W.S., Thodos, George, *Ibid.*, **6**, 240 (1961).
(5) Hilsenrath, Joseph, Touloukian, Y.S., *Trans. Am. Soc. Mech. Engrs.* **76**, 967 (1954).
(6) Keyes, F.G., *J. Am. Chem. Soc.* **53**, 965 (1931).
(7) Kestin, J., Leidenfrost, W., *Physica* **25**, 537 (1959).
(8) Kiyama, Ryo, Makita, Tadashi, *Rev. Phys. Chem. Japan* **22**, 49 (1952).
(9) *Natl. Bur. Std., (U. S.), Circ.* **142**, (1945).
(10) Pinevich, G., *Kholodil'n Tekhn.* **20**, 30 (1947).
(11) Reamer, H.H., Cokelet, G., Sage, B.H., *Anal. Chem.* **31**, 1422 (1959).
(12) Rode, J.S., Reamer, H.H., Sage, B.H., *Rev. Sci. Instr.* **24**, 362 (1953).
(13) Sage, B.H., Lacey, W.N., *Trans. AIME* **136**, 136 (1940).
(14) Shatenshtein, A.I., Izrailevich, E.A., Ladyshnikova, N.I., *Zh. Fix. Khim.* **23**, 497 (1949).
(15) Shimotake, Hiroshi, "Viscosity of Ammonia in the Dense Phase Region: Pressures up to 5000 PSI and Temperatures of 100, 150, and 200° C.," Ph.D. thesis, Northwestern University, Evanston, Ill., 1960, (University Microfilms, Inc., Ann Arbor, Michigan and London, England).
(16) Shimotake, Hiroshi, Thodos, George, *A.I.Ch.E.J.* **9**, 68 (1963).
(17) Stakelbeck, H.Z., *Z. Ges. Kälte-Ind.* **40**, 33 (1933).

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