16-Halohexadecanoic Acids

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AS PART OF STUDY of the surface activity of long-chain alkanoic acids, a series of 16-halohexadecanoic acids was required. Since it was important that the compounds be free of branched isomers and halogen substitution other than at the terminal carbon atom, our synthetic approach was based on the sodium borohydride cleavage of the ozonide (*2*) of 16-heptadecenoic acid to give 16-hydroxyhexadecanoic acid. Under the mild conditions of this reaction, little rearrangement would be expected. The hydroxy acid was readily converted to the corresponding halogen acids (Table I) by conventional procedures.

The 16-heptadecenoic acid was prepared by the reduction of 7-oxo-16-heptadecenoic acid (*3*) in a manner similar to that reported by Brace (*1*) after completion of our work. It was shown recently by Sisido and Kawanisi (*4*) that the usual Wolff-Kishner reaction modifications result in extensive double bond migration during the reduction of unsaturated keto acids. As indicated by Brace (*1*), we also found that a shortened heating period for decomposition of the hydrazone gave the unsaturated acid without rearrangement.

Table I. 16-X-Hexadecanoic Acids

			Analysis							
			Calcd.				Found			
X	Yield %	M.P. ° C.	C	H	X	Neut. Eq.	C	H	X	Neut. Eq.
OH	55	92–93	70.54	11.84	. . .	. . .	70.20	12.10	. . .	. . .
Cl[a]	74	61–61.5	66.07	10.74	12.19	290.9	66.18	10.95	11.99	288.2
Br[b]	66	69.5–70.0	57.31	9.32	23.83	335.3	57.46	9.62	23.46	333.5
I[c]	62	74–74.5	50.26	8.17	33.19	382.3	50.75	8.00	33.25	384.2

[a] From the hydroxy acid, $SOCl_2$, and pyridine. [b] From the hydroxy acid and 48% aq. HBr in acetic acid. [c] From the bromo acid and NaI; all three halogen compounds were recrystallized from light petroleum ether.

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Viscosity of Hydrocarbons. *n*-Butane

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THE VISCOSITY of *n*-butane has been investigated in some detail. Early measurements by Titani (*13*) provided information concerning the viscosity of *n*-butane at temperatures between 68° and 248° F. at atmospheric pressure. Swift and co-workers (*12*) reported on the viscosity of *n*-butane bubble point liquid at temperatures from 68° to 212° F. Lipkin (*5*) also reported data on the viscosity of saturated liquid *n*-butane at temperatures between −100° and 100° F. Starling *et al.* (*11*) described investigations of the viscosity of *n*-butane in the critical region including isotherms at 306°, 307°, and 309° F. Sage (*9*) investigated the effect of pressure on the viscosity of *n*-butane at pressures up to 2000 p.s.i.a. at a temperature interval between 100° and 220° F. for the liquid and gas phases. These latter data were obtained with a rolling-ball viscometer, and unexpected uncertainties exist concerning the reported viscosities in the gas phase at elevated pressures. More recently, Dolan and co-workers (*2*) reported information about the viscosity of *n*-butane at a number of temperatures in the liquid and gas phases at pressures up to 8000 p.s.i.a. at 100° F. and to 1000 p.s.i.a. at 340° F. These data were obtained with a capillary-tube viscometer (*3*).

It is believed that before confidence can be placed in viscosity measurements, data should be obtained over the range of temperatures and pressures of interest from two widely different types of instruments. With this in view measurements of the viscosity of *n*-butane were undertaken to strengthen confidence in the values reported by Dolan (*2*), whose investigation appears to be the most complete

Limited investigations of the viscosity of *n*-butane were carried out at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 320° F. The measurements were used to corroborate the values reported in a more extensive investigation made with an entirely different type of instrument. For the most part, good agreement between the two sets of investigations was found. The current data indicate a smaller effect of pressure upon the viscosity of *n*-butane gas at 100° and 160° F. and a lower viscosity at atmospheric pressure than were found earlier.

to data. Further, at the higher temperatures Dolan's data did not extend to pressures above 1000 p.s.i.a. Data are herein reported at temperatures between 40° and 320° F. and at pressures up to 5000 p.s.i.a. Detailed measurements were not made in portions of the liquid region since good agreement was obtained with Dolan's data at temperatures of 100° and 280° F.

METHODS AND EQUIPMENT

A rotating-cylinder viscometer was employed for these measurements. Methods were the same as those used in the authors' study of ethane (*1*). Details of the apparatus have been presented (*6*), and the modifications found desirable in the equipment were reported (*1*). In principle, the equipment involved a rotating cylinder within which a stator was suspended by a small platinum tungsten wire 0.0065 inch in diameter. Measurements of the angular displacement of the stator as a result of the rotation of the outer cylinder at a predetermined rate permitted the viscosity to be evaluated from the dimensions of the instrument and from the elastic characteristics of the suspension. These elastic characteristics were determined from the natural period of the stator in vacuum.

The angular displacement of the stator was determined by means of angular transducers (*1*). Measurements were made with the cylinder rotating in each direction. The speed of the outside cylinder was established by a predetermined counter driven by a quartz oscillator (*7*) and is known within 0.01%, while the elastic characteristics of the suspension are known within 0.1%. The influence of temperature upon these elastic properties was established by Rode (*8*), and was checked by determining the period in vacuum of the stator at several different temperatures. The dimensions of the stator and the rotating cylinder were checked periodically, and were sufficiently stable that the gap between the stator and the rotating cylinder did not change more than 0.1% within a one-year period.

In order to insure that the over-all behavior of the instrument did not change with time, the viscosity of helium was measured before and after the measurements reported. The results indicate that the viscosity of helium at 100° F. as established from the dimensions of the instrument was 0.4266×10^{-6} lb. sec./sq. ft. or 204.2 micropoises before the primary investigation and 0.4261×10^{-6} lb. sec./sq. ft. or 204.0 micropoises after the investigation. These data agree within 0.1% with the values reported by Kestin and Leidenfrost (*4*) of 0.4267×10^{-6} lb. sec./sq. ft. or 204.3 micropoises. The data here reported for helium were based entirely upon the dimensions of the instrument, the elastic properties of the suspension, and a knowledge of the speed of rotation of the outer cylinder and the angular displacement of the stator.

It is believed that the experimental values reported do not involve uncertainties greater than 0.5%. Although the elastic properties of the suspension changed approximately 1.6% over a two-year period after installation, they remained nearly invariant during the eight months prior to and during the primary set of measurements.

Table I. Experimental Measurements for *n*-Butane

Pressure P.S.I.A.	Viscosity Micropoise	Pressure P.S.I.A.	Viscosity Micropoise	Pressure P.S.I.A.	Viscosity Micropoise
		Series I[a]			
40° F.		100° F.		280° F.	
17.7	68.66	17.5	77.09	18.8	101.84
17.7	68.80	17.5	77.23	18.8	101.84
17.7	68.85	17.5	77.32	18.8	102.08
33.2	1944.84	29.9	77.09	81.0	102.60
33.2	1946.09	29.9	77.09	81.0	102.70
33.2	1941.68	29.9	76.94	81.3	102.60
101.9	1950.73	40.7	77.18	160.4	104.38
101.8	1946.23	39.9	77.09	160.4	104.18
101.9	1946.38	39.8	77.04	160.6	104.28
598.4	2022.22			239.5	106.91
598.8	2022.46	s[c]	0.10	239.6	107.06
597.6	2015.56			239.6	106.29
599.8	2015.80	160° F.		320.0	107.15
599.4	2016.23			320.0	112.04
997.1	2077.90	18.4	85.70	320.3	112.04
998.4	2080.20	19.2	84.75	397.2	123.24
1888.2	2231.11	19.2	84.99	397.2	123.38
1907.5	2224.79	19.2	85.37	397.5	123.14
3004.8	2385.09	40.8	86.18	420.9	130.18
3009.1	2391.08	40.8	86.18	420.9	129.94
3918.0	2495.93	41.3	85.94	421.3	129.99
3931.8	2508.62	78.1	85.80	504.2	502.15
4542.6	2608.88	111.7	86.52	503.9	503.30
4559.2	2615.53	111.7	86.66	603.4	538.64
4881.7	2655.51	111.7	86.42	603.4	538.83
4900.2	2666.14				
4913.6	2647.04	s[c]	0.24		
s[c]	3.93				
				Series II[b]	
280° F.		320° F.		100° F.	
800.6	586.95	29.9	107.82	16.7	76.84
800.4	592.31	29.9	107.68	16.7	76.75
1008.6	639.52	196.4	110.79	16.6	76.80
1008.0	636.50	197.2	110.74	16.5	76.70
1508.3	719.86	399.7	121.76	16.8	77.13
1508.1	721.58	399.9	122.71	16.8	77.56
2006.0	789.57	437.7	126.30	16.4	76.46
2005.8	789.38	437.8	126.35		
2995.8	900.89	477.9	132.34	s[c]	0.33
3000.8	902.52	478.1	132.48		
3927.0	1001.58	478.1	132.48	280° F.	
3938.8	1009.05	511.6	139.42		
3938.8	1005.60	511.6	139.71	16.7	101.79
4491.3	1058.75	511.6	139.90	16.7	101.93
4504.4	1059.23	559.2	155.70		
4504.4	1057.17	558.8	155.85	s[c]	0.10
5122.1	1113.95	558.6	156.61		
5129.3	1113.38	599.3	186.25	400° F.	
5129.3	1113.43	599.3	189.12		
		600.8	187.59	19.7	119.08
s[c]	0.91	640.8	288.28	18.9	119.41
		640.8	290.91	18.9	119.36
		640.8	293.88		
				s[c]	0.14
		s[c]	3.02		

[a] Series I measurements made in 1962. [b] Series II supplementary measurements made in 1963. [c] Average standard deviation expressed in micropoise.

$$s = \left(\left\{ \sum_{1}^{N} (\eta_{\mathrm{av}} - \eta_{\mathrm{e}})^2 \right\} / N \right)^{1/2}$$

MATERIAL

The *n*-butane used in this investigation was obtained from the Phillips Petroleum Co. as research-grade material, and was reported to contain less than 0.001 mole fraction of material other than *n*-butane. Measurements indicated a change in vapor pressure at 100° F. from a quality of 0.10 to 0.80 of 0.06 p.s.i. These measurements confirm the fact that the purity of this sample of *n*-butane was greater than 0.999 mole fraction. Conventional high-vacuum techniques were employed to introduce the material into the viscometer.

EXPERIMENTAL RESULTS

Table I records the experimental measurements of the viscosity of *n*-butane. The values reported for each state represent the average of three angular displacements which were obtained with different speeds of rotation. The standard deviation of these replicate data has been included for each state in Table I and represents the deviation from the linear average value of all measurements made at a single state, as indicated in a footnote.

Figure 1 portrays the effect of pressure upon the viscosity of *n*-butane in the gas phase for temperatures between 40° and 320° F. The standard error of estimate for these data was 0.0018×10^{-6} lb. sec./sq. ft. or 0.86 micropoise. Figure 2 presents similar information for the liquid phase, with a standard error of estimate of 0.0244×10^{-6} lb. sec./sq. ft. or 11.7 micropoises.

Table II records values of the viscosity of *n*-butane in the gas and in the liquid phase for even values of pressure and temperature. These data were taken from the smooth curves shown in Figures 1 and 2.

Figure 3 depicts the variations in the viscosity of *n*-butane with respect to temperature at atmospheric pressure. Included for comparison are the data of Dolan (*2*), Sage (*9*), Starling (*10*), and Titani (*13*). Dolan's data are somewhat higher than the other measurements. Good agreement was found between the earlier measurements by Titani at atmospheric pressure and the data reported by Sage (*9*) for the same pressure. The standard error of estimate has been included for each of these auxiliary investigations as well as for the present measurements. Because of the large disagreement with the recent measurements of Dolan (*2*), a second series of measurements was made at atmospheric pressure. This involved a different sample of *n*-butane of the same reported purity and a new calibration of the instrument. The results were in good agreement with the first set made several months earlier.

Table II. Viscosity of *n*-Butane

Pressure P.S.I.A.	Temperature, ° F. 40	100	160	280	320
	(17.7)[a]	(51.5)	(120.6)	(436.0)	
Dew Point	68.95	77.13	86.90	132.15	
Bubble Point	1922.8	...	...	463.5	
14.7	68.75[b]	77.09	85.32	101.84	107.34
200	1953.94	...	...	105.24	110.84
400	1988.41	...	...	124.20	122.43
600	2022.38	...	...	538.64	187.69
800	2056.88	...	...	592.26	...
1000	2089.92	...	...	635.83	...
1500	2170.36	...	...	721.06	...
2000	2247.44	...	...	788.09	...
2500	2320.22	...	...	846.02	...
3000	2391.08	...	...	903.48	...
3500	2463.37	...	...	958.54	...
4000	2534.24	...	...	1012.16	...
4500	2604.14	...	...	1059.08	...
5000	2671.17	...	...	1103.13	...

[a] Values in parentheses represent vapor pressure expressed in p.s.i.a.
[b] Viscosity expressed in micropoise.

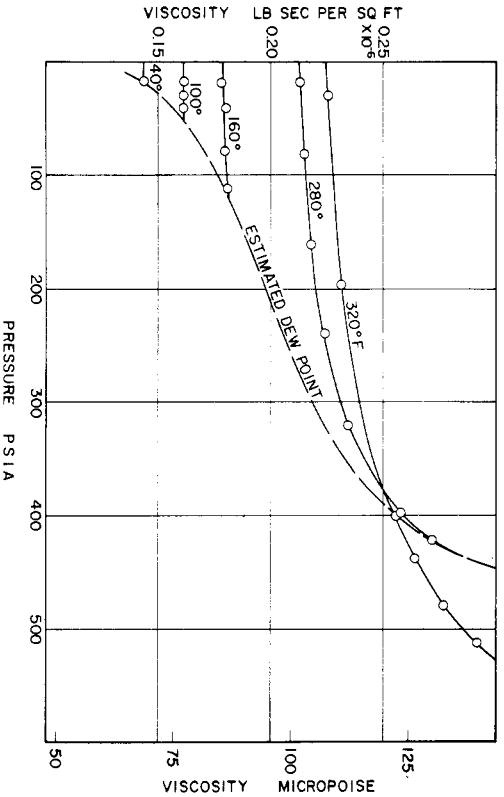

Figure 1. Viscosity of gaseous *n*-butane

A comparison of the viscosities at atmospheric pressure for *n*-butane and helium is presented in Table III. The agreement at low temperatures with the measurements of Dolan is not entirely satisfactory. However, at 400° F. somewhat better agreement was obtained. Starling's data (*10*) are in satisfactory agreement with present measurements except at 400° F.

Figure 4 presents a comparison of data on the viscosity of *n*-butane in the gas phase as reported by Dolan (*2*), Sage (*9*), and Starling (*10, 11*) with data from the present investigation. The smooth curves represent the current data, with the standard error of estimate of the values from each of the other investigators included for comparison. The trends of the earlier measurements (*9*), which were made with the rolling-ball viscometer, and the current data are in poor agreement except at atmospheric pressure. In the case of the rolling-ball viscometer, the increase in Reynolds number with increase in pressure yielded turbulent wakes behind the ball with an attending apparent rapid increase in viscosity.

Figure 5 presents a similar comparison of the viscosity of the liquid phase up to 1000 p.s.i.a. including the measurements of Lipkin (*5*) and Swift (*12*) for the saturated liquids. Agreement with Dolan's measurements (*2*) was considered satisfactory, and reasonable agreement was found with the earlier rolling-ball-viscometer measurements (*9*). The data of Lipkin and Swift agree with the values recommended by Dolan and with the current measurements within the reported uncertainty of measurement.

Figure 6 shows the "residual viscosity," which is defined as the difference between the viscosity at a given state and at attenuation for the same temperature as a function of specific weight for *n*-butane. The behavior at low pressure

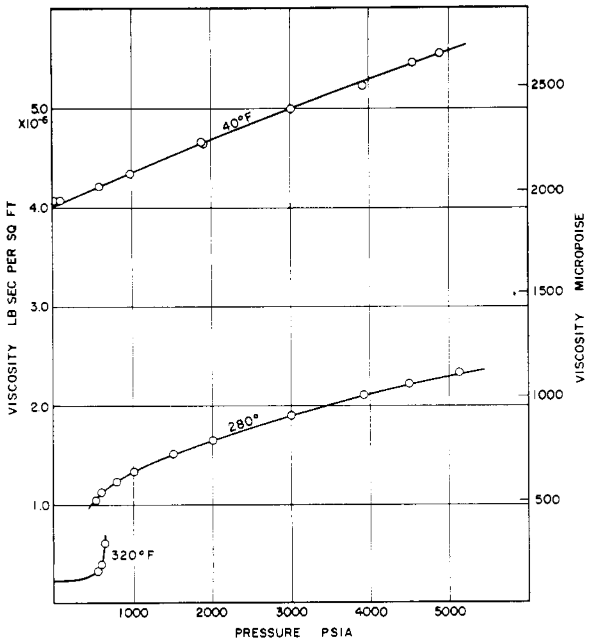

Figure 2. Viscosity of *n*-butane in the liquid and dense phases

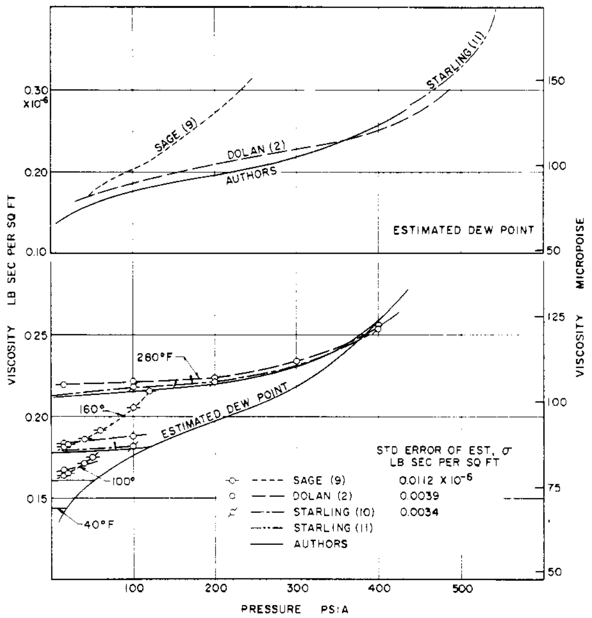

Figure 4. Comparison of data from several investigators

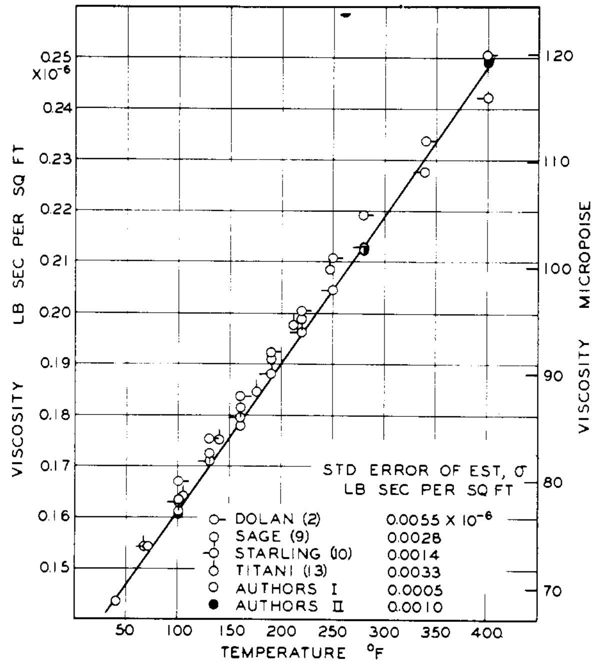

Figure 3. Viscosity of *n*-butane at atmospheric pressure

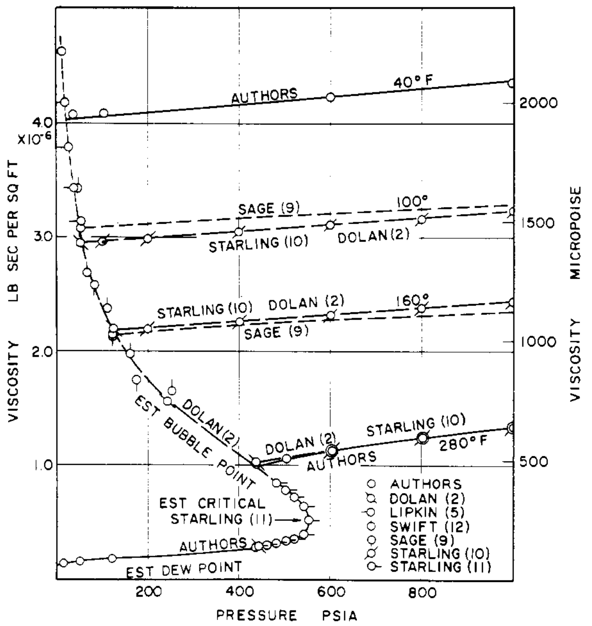

Figure 5. Comparison of data from several investigators in the liquid phase

Table III. Comparison of Viscosity at Atmospheric Pressure

Source	40	100	160	280	400	100
	n-Butane					Helium
Authors I[a]	68.75[b]	77.23	85.22	101.93	...	204.0
Authors II[c]	...	76.89	...	101.89	119.27	203.6
Dolan (*2*)[d]	...	80	88	105	120	
Sage (*9*)	...	78.4	86.9	...	...	
Starling (*10*)[e]	...	78	86	102	116	
Kestin (*4*)						204.3

Temperature, ° F.

[a] Measurements during August and December 1962. [b] Viscosity expressed in micropoise. [c] Measurements during February and March 1963. [d] "Recommended" values (*2*). [e] Interpolated from (*10*).

is shown on an enlarged scale in the upper part of the figure. The results appear to indicate that the residual viscosity is a single-valued function of specific weight within the experimental uncertainty of measurement. The experimental data yielded a standard error of estimate of 0.0266 × 10^{-6} lb. sec./sq. ft. or 12.7 micropoises from the single curve drawn through the data.

A similar diagram is shown in Figure 7, where the data of Dolan (*2*) and Starling (*10*) have been presented for comparison with the present measurements. A standard error of estimate of 0.0092 × 10^{-6} lb. sec./sq. ft. or 4.4 micropoises was found for Dolan's data from the full curve representing the present data. No trends were encountered for a temperature dependence of the residual viscosity of *n*-butane at low specific weights. Such behavior was, however, reported for ethane (*1*).

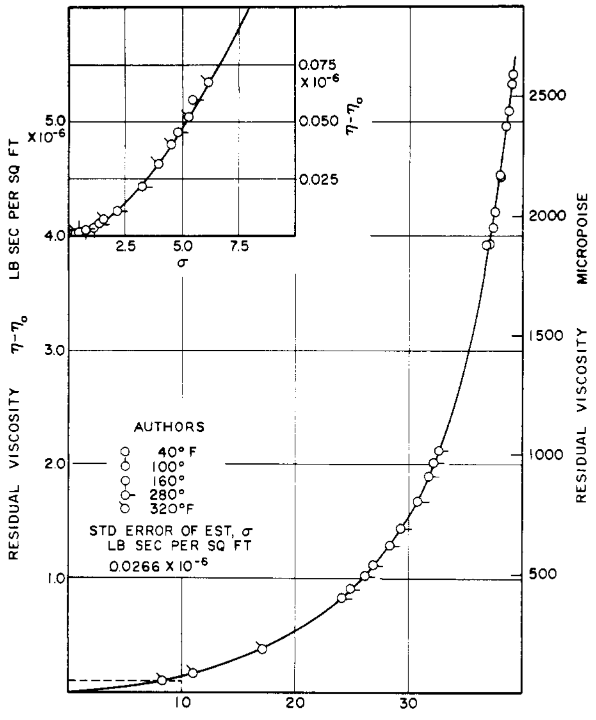

Figure 6. Residual viscosity of *n*-butane

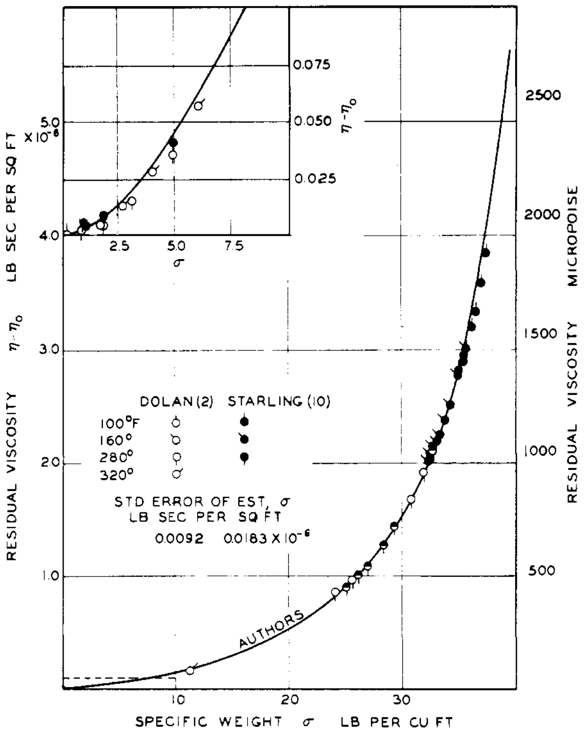

Figure 7. Residual viscosity from data of several investigators

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NOMENCLATURE

N = total number of experimental points
s = average standard deviation
η = viscosity, lb. sec./sq. ft. or micropoise
$\sum$ = summation operator
σ = specific weight, lb./cu. ft.
σ = standard error of estimate

Subscripts

av = average or mean value
e = experimental
n = number of experimental points in a set
o = attenuation

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