

Table II. Coefficients of Eq 3 for Tetrachloromethane^a

T/K	a ₀ /MPa	a ₁	-a ₂ /GPa ⁻¹	a ₃ /GPa ⁻²	δK/%
308.15	981.425 25	1.490 071	-36.327 9	-144.298 1	0.55
318.15	830.976 43	4.743 49	3.819 29	2.244 47	0.06
338.15	700.553 04	4.848 12	4.992 63	5.318 30	0.07

^aThe average deviation in K in column 6 (see eq 3) corresponds to roughly $1/10$ that deviation in the volume ratio.

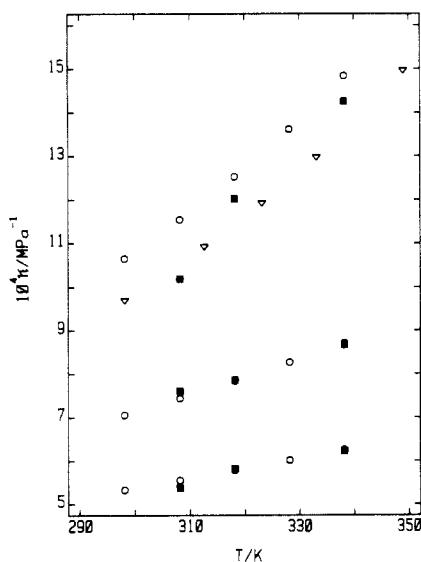


Figure 1. Isothermal compressibility of carbon tetrachloride: uppermost values, 0.1 MPa; middle, 50 MPa; bottom, 100 MPa; circles, ref 1; squares, this work; triangles, ref 7.

Table I. The agreement between the two sets of values is generally excellent although the volume ratios presented here are consistently slightly higher than those calculated from ref 1. It is of some interest to note that if eq 2 is used (with the coefficients from ref 1) to calculate volume ratios above 100 MPa (the highest pressure used in ref 1), there is still excellent agreement with the present data up to 150 MPa at all three temperatures.

Although equations of the form of eq 2 provide a reliable method of extrapolating outside the pressure range of the measurements they represent, such equations do not fit the measured volume ratios as well as secant bulk modulus equations, usually of third order, of the form

$$K = p/(1 - k) = \sum_{i=0}^n a(i)p^i \quad (3)$$

Coefficients of eq 3 which provide a good fit to the present results are given in Table II.

Isothermal compressibilities, κ , can be obtained from the volume ratios since

$$\begin{aligned} \kappa &= -(1/V)(\partial p)_T = -(1/k)(\partial k/\partial p)_T \\ &= -(1/(p - K))(1 - (p/K)(\partial K/\partial p)_T) \end{aligned} \quad (4)$$

Values of κ obtained from eq 3 and 4 are shown in Figure 1 where they are compared with those obtained from Gibson and Loeffler (1) (eq 1 and 4) and Holder and Whalley (7). Overall there is the expected close agreement between κ from the present measurements and those from Gibson and Loeffler; the greatest difference is found at 308.15 K. The systematic difference from Holder and Whalley is difficult to explain although it should be remembered that the present data and those of ref 1 are less accurate the lower the pressure and that both Gibson and Loeffler and Holder and Whalley used mercury to transmit the pressure.

Registry No. Tetrachloromethane, 56-23-5.

Literature Cited

- (1) Gibson, R. E.; Loeffler, O. H. *J. Am. Chem. Soc.* **1941**, *63*, 898.
- (2) Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* **1931**, *66*, 185.
- (3) Back, P. J.; Easteal, A. J.; Hurle, R. L.; Woolf, L. A. *J. Phys. E: Sci. Instrum.* **1982**, *15*, 360.
- (4) Easteal, A. J.; Woolf, L. A. *J. Chem. Thermodyn.* **1985**, *17*, 49.
- (5) Machado, J. R. S.; Street, W. B. *J. Chem. Eng. Data* **1983**, *28*, 218.
- (6) Eduljee, H. E.; Newitt, D. M.; Weale, K. E. *J. Chem. Soc.* **1951**, 3086.
- (7) Holder, G. A.; Whalley, E. *J. Chem. Soc., Faraday Trans. 1* **1962**, *58*, 2095.

Received for review June 14, 1985. Accepted December 16, 1985.

Vapor Pressures of Poly(dimethylsiloxane) Oligomers

Ora L. Flaningam

Analytical Research Laboratory, Dow Corning Corporation, Midland, Michigan 48640

Vapor pressures of seven linear, seven cyclic, and two branched dimethylsiloxane oligomers have been measured over the pressure range 7–133 kPa (50–1000 Torr). The experimental data were fitted by the Antoine equation. Extrapolations of these data to the critical point were made by using literature or estimated critical constants and the Halm–Stiel extension of Pitzer's vapor pressure equation. Constants for the Halm–Stiel equation are given. The extrapolated data were also fit to the AIChE DIPPR vapor pressure equation.

Introduction

For engineering calculations we required vapor pressure of low molecular weight cyclic, linear, and branched poly(dimethylsiloxanes). Data were necessary which extend to the

critical point. Critical points are known for many of these oligomers, but vapor pressure data near the critical have been measured for only two. Also, examination of the literature showed remarkable variations in the reported vapor pressure for all of them (1–18). For these reasons we have remeasured vapor pressure for the linear compounds from hexamethyl-disiloxane through hexadecamethyloctasiloxane, cyclic compounds from hexamethylcyclotrisiloxane through octadecamethylcyclononasiloxane, and the two branched compounds methyltris(trimethylsiloxy)silane and tetrakis(trimethylsiloxy)silane. No literature vapor pressure data were found for the branched compounds.

Because all of these compounds have very long names, the system of abbreviation introduced by Wilcock (1) will be used. All of the compounds can be said to be made up of four structural groups, the monofunctional trimethylsiloxy group, $(\text{CH}_3)_3\text{SiO}_{1/2}$ (M), the difunctional dimethylsiloxy group, $(\text{CH}_3)_2\text{SiO}$

(D), the trifunctional $\text{CH}_3\text{SiO}_{3/2}$ (T) group, and the quaternary functional group SiO_2 (Q). It should be kept in mind that half of each attached oxygen group is included in each unit. Thus, hexamethyldisiloxane can be represented by MM, decamethyltetrasiloxane by MD_2M , hexamethylcyclotrisiloxane by D_3 , methyltris(trimethylsiloxy)silane by TM_3 , tetrakis(trimethylsiloxy)silane by QM_4 , etc. TM_3 is the branched isomer of MD_2M while QM_4 is the branched isomer of MD_3M .

Experimental Section

All of the compounds were obtained from distillations through a high-efficiency distillation column. The linear siloxanes and QM_4 were distilled from 0.65, 1, 1.5, 3, and 5 cSt Dow Corning 200 Fluids. The cyclic trimer was resublimed after having been distilled. The lower cyclics were distilled from plant cyclics. The cyclic heptamer (D_7) and octamer (D_8) were supplied by Lane. The cyclic nonamer (D_9) was obtained from distillation of macrocyclics prepared by Hampton. The TM_3 was obtained from Silar Laboratories and was used as received.

The distillation column was a 3 ft by 1 in. vacuum jacketed column packed with Podbielniak stainless steel helices. It has been tested at 50–60 theoretical plates when operated at 1 atm and reflux rates greater than 100 to 1. For the materials boiling above 473 K, the distillation was done under vacuum at 2670 Pa (20 Torr).

Except for D_9 , all were known to be 99% pure or better by gas chromatographic analysis. Sample purity was determined by using an HP 5880 gas chromatograph connected to an HP 3354 laboratory computer. The GC column was $1/8$ in. by 6 ft stainless steel. It was packed with OV-210, 16% on Chromasorb-P, AW-DMCS, 120 mesh. GC area percent was converted to weight percent by using response factors for known standards. The individual purities are given in the tables. The sample of D_9 was known to decompose in the gas chromatograph and gave variable analyses. It is known to be greater than 95% pure.

The vapor pressure measurements were made in an ebulliometer designed after those reported by Stull (19). A sketch of the apparatus is given in Figure 1. Temperature was measured by a four-terminal platinum resistance thermometer (PRT) connected to a Leeds & Northrup (L&N) G-3 Mueller bridge with mercury commutator, an L&N electronic null detector and recorder. Sensitivity was adjusted so that 0.01-deg variation was easily observable. Temperature readings were to the nearest 0.01 K. The thermometer was calibrated to ± 0.001 K by comparison with an L&N primary standard PRT with calibration traceable to the National Bureau of Standards. Calibration was to the IPTS of 1968. The ebulliometer was connected to the pressure manifold through an 8-L ballast tank which smoothed out pressure variations from the boiling liquid. Pressure was measured by an MKS Instruments Baratron capacitance manometer with 0–133 kPa (0–1000 Torr) range. This instrument was readable to ± 1.3 Pa (0.01 Torr) and was kept within 6.7 Pa (0.05 Torr) of the nominal value during the measuring period. The MKS gauge was calibrated against a Ruska Corp. dead weight gauge with calibration traceable to the NBS. Pressure was adjusted by vacuum pumps and by dry nitrogen.

Measurements were made on water, methylcyclohexane, and diphenyl ether to check the validity of the method. About eight measurements were made on each compound over a range of pressures from 4 to 101 kPa (30–760 Torr). Experimental vapor pressures reproduced literature values (20, 21, 22) to within $\pm 0.07\%$ average vapor pressure error. Average pressure error = $\sum((P_{\text{expt}} - P_{\text{calcd}})/P_{\text{calcd}} \times 100)/N$.

All boiling points are the average of at least three readings at varied heat inputs to assure that the temperature is not below the true boiling point and the sample is not superheated. The

Table I. Hexamethyldisiloxane (MM)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
302.78	6.93	6.95	352.90	53.27	53.34
303.81	7.33	7.31	359.76	66.60	66.68
308.89	9.33	9.33	365.61	79.94	79.99
310.36	9.99	10.00	373.56	101.28	101.28
311.73	10.66	10.65	373.59	101.33	101.37
316.71	13.32	13.32	379.50	119.91	119.84
326.24	19.98	19.96	383.30	133.15	133.01
333.47	26.63	26.58			

Table II. Octamethyltrisiloxane (MDM)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
346.10	6.69	6.69	402.77	53.25	53.27
355.49	10.02	10.02	410.37	66.65	66.60
362.57	13.35	13.34	416.86	79.92	79.93
373.22	20.00	19.99	425.70	101.29	101.36
381.30	26.65	26.65	432.25	119.96	119.91
393.48	39.94	39.95	436.49	133.26	133.25

Table III. Decamethyltetrasiloxane (MD_2M)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
366.20	3.36	3.36	432.88	39.94	39.94
370.16	4.03	4.02	442.87	53.25	53.25
376.66	5.36	5.36	451.05	66.65	66.58
381.92	6.69	6.69	458.06	79.92	79.96
392.05	10.02	10.04	467.55	101.29	101.33
399.60	13.35	13.33	474.64	119.96	119.99
411.10	20.00	20.00	479.17	133.26	133.23
419.76	26.65	26.64			

Table IV. Dodecamethylpentasiloxane (MD_3M)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
395.61	3.36	3.36	476.94	53.25	53.25
399.81	4.03	4.02	485.61	66.65	66.59
406.69	5.36	5.35	492.99	79.92	79.90
412.31	6.69	6.69	503.04	101.29	101.28
423.05	10.02	10.03	503.07	101.29	101.35
431.11	13.35	13.35	510.55	119.96	119.97
452.47	26.65	26.64	515.36	133.26	133.28
466.36	39.94	39.94			

Table V. Tetradecamethylhexasiloxane (MD_4M)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
449.17	10.02	10.00	514.58	66.65	66.46
457.76	13.35	13.37	522.25	79.92	79.68
470.38	20.00	19.98	532.95	101.29	101.48
480.11	26.65	26.71	540.75	119.96	120.09
494.59	39.94	39.99	545.71	133.26	133.24
505.63	53.25	53.29			

range of temperatures in such a series of readings was always less than 0.1 K and usually within 0.05 K.

Results and Discussion

The experimental results are given in Tables I–XVI. A least-squares fit was made to the Antoine equation

$$\ln(P) = A - B/(T + C) \quad (1)$$

where pressure is given in pascals, temperature is in degrees

Table VI. Hexadecamethylheptasiloxane (MD₇M)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
443.87	3.36	3.34	505.86	26.65	26.65
448.73	4.03	4.04	520.80	39.94	39.95
456.28	5.36	5.38	532.12	53.25	53.24
462.30	6.69	6.69	541.37	66.65	66.57
467.47	8.02	8.03	549.27	79.92	79.95
473.93	10.02	10.01	559.85	101.29	101.12
474.00	10.02	10.03	559.96	101.29	101.36
482.78	13.35	13.35	559.79	101.29	100.99
495.89	20.00	19.98	568.06	119.96	120.43

Table VII. Octadecamethyloctasiloxane (MD₈M)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
464.71	3.36	3.36	527.95	26.65	26.65
469.39	4.03	4.03	543.25	39.94	39.91
477.09	5.36	5.36	554.93	53.25	53.26
483.31	6.69	6.69	564.52	66.65	66.70
495.26	10.02	10.01	572.73	79.92	80.23
504.23	13.35	13.33	583.48	101.21	101.15
517.77	20.00	20.01	585.87	106.63	106.33

Table VIII. Hexamethylcyclotrisiloxane (D₃)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
342.62	10.68	10.68	386.38	53.25	53.24
347.93	13.35	13.35	393.64	66.58	66.57
358.15	20.00	20.00	399.84	79.92	79.92
365.88	26.65	26.66	408.25	101.29	101.30
372.17	33.29	33.30	412.38	113.30	113.32
377.52	39.94	39.94	416.58	126.62	126.64
377.51	39.94	39.93	419.67	137.23	137.19
382.20	46.59	46.59			

Table IX. Octamethylcyclotetrasiloxane (D₄)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
361.71	5.36	5.35	424.99	53.25	53.26
366.76	6.69	6.69	432.78	66.65	66.55
376.41	10.02	10.02	439.46	79.92	79.91
383.69	13.35	13.35	448.53	101.29	101.31
394.63	20.00	19.99	455.29	119.96	119.95
402.94	26.65	26.66	459.65	133.26	133.31
415.46	39.94	39.96			

Table X. Decamethylcyclopentasiloxane (D₅)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
383.76	4.06	4.06	458.14	52.65	52.64
399.61	7.81	7.82	475.17	81.76	81.74
414.17	13.46	13.46	484.19	101.53	101.54
435.10	26.96	26.97	496.05	132.98	132.99

Table XI. Dodecamethylcyclohexasiloxane (D₆)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
411.70	4.13	4.13	489.26	50.93	50.93
428.63	7.95	7.95	503.03	71.65	71.60
444.24	13.73	13.69	514.53	93.62	93.47
458.82	21.69	21.76	520.36	106.10	106.38
469.56	29.85	29.87	531.56	135.10	134.99

Table XII. Tetradecamethylcycloheptasiloxane (D₇)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
431.27	3.36	3.36	493.21	26.65	26.65
435.83	4.03	4.03	508.38	39.94	39.92
443.32	5.36	5.36	519.99	53.25	53.25
449.40	6.69	6.69	529.51	66.65	66.59
461.07	10.02	10.02	537.65	79.92	79.95
469.89	13.35	13.35	548.08	99.95	100.02
483.14	20.00	20.00	548.67	101.29	101.27

Table XIII. Hexadecamethylcyclooctasiloxane (D₈)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
454.07	3.36	3.36	508.01	20.00	19.97
458.77	4.03	4.02	508.09	20.00	20.01
466.57	5.36	5.36	534.40	39.94	39.96
472.89	6.69	6.69	546.46	53.25	53.25
494.27	13.35	13.35	564.83	79.92	79.93
494.27	13.35	13.35	576.32	101.29	101.26

Table XIV. Octadecamethylcyclononasiloxane (D₉)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
473.14	3.36	3.37	539.44	26.66	26.67
477.94	4.03	4.03	548.26	33.29	33.35
485.84	5.36	5.34	555.77	39.94	40.04
492.40	6.69	6.67	562.29	46.59	46.67
504.95	10.02	10.01	568.07	53.25	53.25
514.41	13.35	13.34	578.12	66.65	66.42
528.66	20.00	20.01			

Table XV. Methyltris(trimethylsiloxy)silane (TM₃)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
362.79	3.33	3.32	407.91	19.95	19.97
366.78	3.99	3.99	416.59	26.61	26.60
373.34	5.32	5.32	429.68	39.93	39.86
373.34	5.32	5.32	439.68	53.24	53.17
378.62	6.64	6.65	447.87	66.55	66.51
378.63	6.64	6.65	464.40	101.30	101.34
388.74	9.97	9.97	464.40	101.30	101.34
388.77	9.97	9.98	471.50	119.93	120.05
396.40	13.30	13.30	476.03	133.31	133.31

Table XVI. Tetrakis(trimethylsiloxy)silane (QM₄)

T/K	vapor press./kPa		T/K	vapor press./kPa	
	measd	calcd		measd	calcd
398.15	5.30	5.30	444.05	26.63	26.62
403.87	6.66	6.66	458.00	39.95	39.95
414.58	9.99	9.99	468.62	53.27	53.27
422.68	13.32	13.33	468.60	53.27	53.24
422.69	13.32	13.33	484.76	79.94	79.94
434.83	19.98	19.97	494.87	101.28	101.30

kelvin, and A , B , and C are constants. Vapor pressures calculated from these constants are given in Tables I–XVI. Table XVII is a summary of Antoine constants for all 16 compounds. The calculated normal boiling point, standard deviation of experimental temperature and pressure, experimental temperature and pressure range, and sample purity are also given.

A comparison of our data with literature values was done by plotting the percent pressure deviation from some standard vapor pressure vs. the temperature. Such a plot is given in Figure 2 for hexamethyldisiloxane. The reference for com-

Table XVII. Summary of Antoine Constants for Poly(dimethylsiloxanes)

compd	Antoine constants ^a			calcd bp/K	std dev		exptl range		% purity
	A	B	C		T/K	P/kPa	T/K	P/kPa	
MM	20.1601	2580.44	-74.705	373.57	0.04	0.057	300-383	6.9-133	99.90
MDM	20.4352	3033.52	-85.190	425.69	0.02	0.032	346-446	6.7-133	99.83
MD ₂ M	20.4183	3253.19	-101.702	469.55	0.04	0.028	366-479	3.4-133	99.26
MD ₃ M	20.5037	3506.62	-112.464	503.06	0.03	0.026	395-515	3.4-133	99.27
MD ₄ M	20.5387	3690.21	-123.430	532.88	0.08	0.123	449-545	10-133	99.64
MD ₅ M	21.0825	4214.80	-118.897	559.94	0.08	0.142	443-468	3.3-119	99.36
MD ₆ M	20.9056	4184.96	-137.381	583.56	0.06	0.121	464-586	3.3-106	99.97
D ₃	20.6062	3001.41	-77.710	408.26	0.03	0.016	342-419	10-137	99.99
D ₄	20.4534	3128.52	-98.093	448.54	0.03	0.034	361-469	5.4-133	99.47
D ₅	20.3178	3292.00	-109.657	484.10	0.03	0.012	383-496	4.0-133	99.70
D ₆	20.4120	3572.15	-116.144	518.15	0.08	0.113	411-531	4.1-135	99.90
D ₇	20.2689	3661.26	-129.926	548.70	0.04	0.031	431-548	3.3-101	99.23
D ₈	20.2731	3816.95	-139.980	576.35	0.05	0.015	454-576	3.3-101	95
D ₉	20.3599	3989.87	-147.070	598.73	0.10	0.078	473-578	3.3-67	99.00
TM ₃	20.4542	3276.24	-97.436	464.70	0.03	0.040	362-476	3.3-133	99.66
QM ₄	20.2751	3355.93	-111.301	494.86	0.03	0.011	398-494	5.3-10	99.97

^a $\ln P_v = A - B/(T + C)$, where P_v is in pascal and T in kelvin.

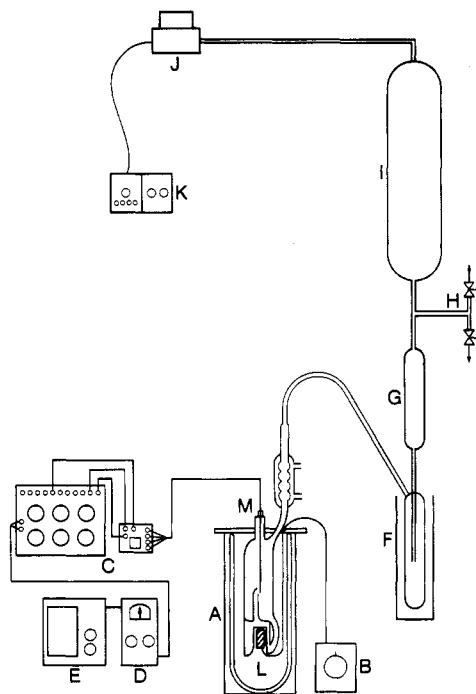


Figure 1. Sketch of the vapor pressure apparatus: A, vapor pressure ebulliometer, (ref 19); B, heater variac; C, resistance thermometer bridge and commutator; D, null detector; E, recorder; F, cold trap; G, drying tube; H, valves to vacuum and nitrogen; I, pressure ballast; J, MKS pressure gauge; K, pressure gauge controller; L, heater; M, platinum resistance thermometer.

parison is the data of Scott and co-workers (3), which we regard as the only highly accurate literature data on any of the compounds. The wide range of variation of the literature (1-9) from this reference is obvious. Most of the data sets show gross systematic error. Our data and those of Guzman are the only ones which show little deviation from the reference. Similar plots were made for all the compounds and the same variations between workers were found in each case. Our data were always near the mean of such variations.

Our data may be extrapolated to the critical point by combining them with vapor pressures near the critical point and with measured or estimated critical constants. This extrapolation was done using the Halm-Stiel (23) extension of Pitzer's (24) corresponding states vapor pressure equation. The Halm-Stiel equation is

$$\log P_r = (\log P_r)^0 + w(\log P_r)^1 + x(\log P_r)^2 \quad (2)$$

where P_r is the reduced vapor pressure, P/P_c . $(\log P_r)^0$, $(\log P_r)^1$, and $(\log P_r)^2$ are tabulated functions (23, 24) of reduced temperature, T/T_c . w is Pitzer's acentric factor; $w = -\log P_{r(T_r=0.7)} - 1.0$; x is the Halm-Stiel polar factor; $x = \log P_{r(T_r=0.6)} - \log P_{m(T_r=0.6)}$. $\log P_m$ is the reduced vapor pressure calculated from the normal fluid equation. The entropy and enthalpy of vaporization can also be calculated from the Halm-Stiel equation. The entropy of vaporization is defined as

$$S = S^{(0)} + wS^{(1)} = xS^{(2)} \quad (3)$$

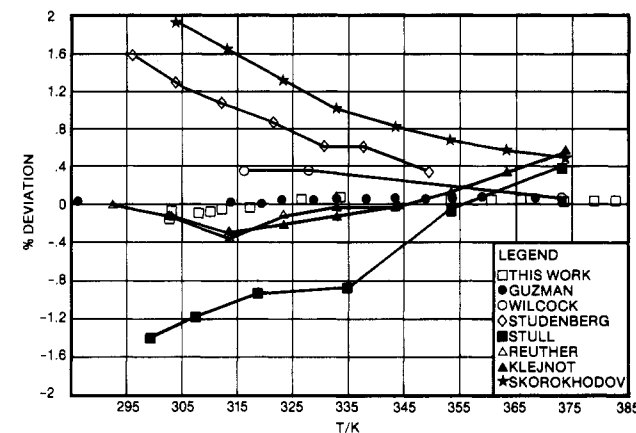


Figure 2. Vapor pressure of hexamethylsiloxane (MM), percent deviation of various workers vapor pressure data from that of Scott et al. (3).

$P_r^{(1)}$, and $(\log P_r)^2$ are tabulated functions (23, 24) of reduced temperature, T/T_c . w is Pitzer's acentric factor; $w = -\log P_{r(T_r=0.7)} - 1.0$; x is the Halm-Stiel polar factor; $x = \log P_{r(T_r=0.6)} - \log P_{m(T_r=0.6)}$. $\log P_m$ is the reduced vapor pressure calculated from the normal fluid equation. The entropy and enthalpy of vaporization can also be calculated from the Halm-Stiel equation. The entropy of vaporization is defined as

$S^{(0)}$, $S^{(1)}$, and $S^{(2)}$ are tabulated functions of reduced temperature (23). The enthalpy of vaporization, H_v is related to the entropy of vaporization by $H_v = T\Delta S$.

Computer programs originally developed by Halm have been rewritten to run on a microcomputer in BASIC language. They were used to calculate P_c , w , and x . The required input is the critical temperature, vapor pressure data points, and a "flag" telling whether the computation should be done assuming the compound is polar or nonpolar. Other data which may be input are normal boiling point, P_c , w , and x . If normal boiling point is given, the correlation will be forced through this point. If any of the other data is given, it is not calculated and is simply used to calculate the output table. The program, thus, has ten options. The object of the fitting procedure is to minimize the root-mean-square error of the calculated from the experimental vapor pressures and to ensure that no systematic error is present.

Vapor pressures near the critical point have been measured for MM (25) and D₄ (26). Experimental critical temperature and pressure have been measured for all the linear compounds

Table XVIII. Experimental Critical Constants for Poly(dimethylsiloxanes) and Tetramethylsilane

compd	T_c		P_c		V_c/mol	ref	
	$^{\circ}\text{C}$	K	atm	MPa			
Me_4Si	(175.49) ^b	448.64	(27.84)	2.821	361	(34)	
	(177.25)	450.4	(27.77)	2.814		(36)	
MM	245.3	(518.45)	25.0 ^a	(2.53)	611	(27)	
	(279.8)	553				(28)	
	(243.45)	516.6	(18.85)	1.910		573.4	(26)
	(243.45)	516.6	(18.85)	1.910		573	(29)
	(245.65)	518.8	(18.85)	1.910		583	(32)
	(245.55)	518.7	(19.00)	1.925			(25)
MDM	291.2	(564.4)	17.0 ^a	(1.72)	868	(27)	
	(309.8)	583				(28)	
	(289.75)	562.9	14.01	(1.420)			(29)
	(292.25)	565.4	14.41	(1.43)		828	(32)
MD ₂ M	326.0	(599.15)	13.0 ^a	(1.32)	1157	(27)	
	(328.8)	602				(28)	
	(326.25)	599.4	12.48	(1.265)		1005	(29)
	(326.25)	599.4	(11.74)	1.19		1208	(32)
MD ₃ M	354.5	(627.6)	10.5 ^a	(1.06)	1400	(27)	
	(349.8)	623				(28)	
	(355.85)	629.0	9.33	(0.945)		1509	(29)
	(380.05)	653.2	7.93	(0.804)		1808	(29)
MD ₄ M	(398.65)	671.8	6.68	(0.677)	2133	(29)	
MD ₅ M	(415.75)	688.9	6.16	(0.624)	2466	(29)	
D ₃	281.0	(554.15)	22.0 ^a	(2.32)	707	(27)	
D ₄	314.2	(587.35)	18.0 ^a	(1.82)	970	(27)	
	(279.85)	553				(28)	
	(313.35)	586.5	13.07	(1.324)		910	(31)
	(313.35)	586.5	13.22	(1.339)		984	(30)
D ₅	346.0	(619.15)	15.0 ^a	(1.52)	1216	(27)	
	(319.85)	593				(28)	
TM ₃	323.8	(596.95)	12.0 ^a	(1.22)	1125	(27)	
QM ₄	350.2	(623.25)	8.2 ^a	(0.83)	1400	(27)	

^a Pollnow's critical pressures were calculated from van der Waals constants. ^b Values not in parentheses are as reported in the literature. Values in parentheses are calculated from the reported value.

(24–32) and for three of the cyclics (25–27, 30). A summary of this data is given in Table XVIII. McLure and Neville (33) have examined the critical properties of the linear siloxanes and have established that tetramethylsilane (Me_4Si) is the natural forerunner of the series. For this reason we have also included a vapor pressure analysis of the literature data for Me_4Si (34, 35) to complete the series and to serve as a comparison of the present work. Examination of Table XVIII reveals that the critical temperature data of Cholpan (28) are inconsistent, and they were not considered. Cholpan did not measure critical pressure. The previously unreported critical temperature data of Pollnow (27) agree well with the literature. His calculated critical pressures are inconsistent and were not considered. His

is the only measurement of critical temperature of D₃, TM₃, QM₄, and except for Cholpan, the only measurement of critical temperature for D₅. The rest of the critical temperature and pressure data are generally in good agreement between investigators. These data were then used to estimate missing critical data and then to calculate the Halm–Stiel equation constants.

As a test of how well the method works, vapor pressure regressions of MM and D₄ were done two ways. Regressions were performed on our data alone, as well as with our data combined with the literature data near the critical (25, 26). Comparisons of these regressions will show how well the extrapolations could be for those compounds which have no vapor pressure data at high temperatures. In these comparisons the agreement between the two regressions was always better than 0.2%. This assumes that the same critical constants are used for both regressions. The closeness of this comparison gives confidence that the extrapolations will be reasonable.

The Lyderson (37, 38) and Eduljee (39, 40) methods were used to estimate critical constants for all of the compounds. In our work with other silicon compounds we have found these methods to give values within the usual error reported for the methods. The estimations are generally correct within ± 5 K for T_c and ± 202 kPa (± 2 atm) for P_c . Estimations of critical temperature have usually proven more consistent than those of critical pressure. For these compounds, however, the reverse was found to be true. The results of estimations of P_c were found to be well within the expected error while the estimations of critical temperature showed very severe systematic errors which increase as the size of the molecule increases.

The best correlation which we have found for prediction of critical temperatures for poly(dimethylsiloxanes) is based on the relationship of T_c to T_b (the normal boiling point). If the ratio T_b/T_c is plotted against the normal boiling point, a linear relationship is found for each family. The relationship for the linears is well established, with seven measured critical temperatures. The cyclic correlation consists of only three compounds, and appears to diverge slightly from the linear correlation. The maximum error for these correlations was 0.3% (1.7 K). The average error for the ten compounds was 0.1 K (standard deviation of 1.1). The results of these calculations are given in Table XIX. It should be noted that the calculated critical temperatures for TM₃ and QM₄ (Table XIX) agreed remarkably well with the experimental values of Pollnow (27) although that data was not used in the correlation.

Figures 3 and 4 show the experimental data and the calculated vapor pressure from the Halm–Stiel equation. The smooth locus formed by the critical points give confidence that the critical point estimations are within reason. The vapor pres-

Table XIX. Estimation of T_c for Poly(dimethylsiloxanes) by T_b/T_c^a vs. T_b

compd	T_b/K	T_c/K	T_b/T_c	$T_b/T_c(\text{calcd})$	$T_c(\text{calcd})$	$T_c(\text{error})$	$T_c(\% \text{ error})$
MM	373.7	518.7	0.7205	0.7222	517.4	-1.3	-0.25
MDM	425.7	564.4	0.7543	0.7532	565.2	0.8	0.14
MD ₂ M	467.5	599.4	0.7799	0.7792	600.7	1.3	0.22
MD ₃ M	503.1	628.4	0.8006	0.7995	629.3	0.9	0.14
MD ₄ M	532.9	653.2	0.8158	0.8173	652.0	-1.2	-0.18
MD ₅ M	599.9	671.8	0.8334	0.8334	671.8	0.0	0.0
MD ₆ M	583.6	688.9	0.8471	0.8477	688.2	-0.7	-0.10
D ₃	409.6	554.2	0.7391	0.7404	553.2	-1.0	-0.18
D ₄	448.6	586.5	0.7649	0.7627	588.2	1.7	0.29
D ₅	484.1	619.2	0.7818	0.7829	618.3	-0.9	-0.15
D ₆	518.2			0.8024	645.8		
D ₇	548.7			0.8198	669.5		
D ₈	576.5			0.8356	689.2		
D ₉	598.7			0.8482	705.8		
TM ₃	464.7	596.9	0.7785	0.7765	598.4	1.5	0.25
QM ₄	494.9	623.2	0.7941	0.7946	622.8	-0.4	-0.06

^a T_b is the boiling point, K. T_c is the critical temperature, K. Linear correlation: $T_b/T_c = 0.4990 + (5.9724 \times 10^{-4})T_b$; correlation coefficient = 0.9995. Ring correlation: $T_b/T_c = 0.5069 + (5.7017 \times 10^{-4})T_b$; correlation coefficient = 0.9957.

Table XX. Halm-Stiel Equation Constants for Poly(dimethylsiloxanes) and Tetramethylsilane

compd	T_c , K	P_c , MPa			
		exptl	calcd	w	x
Me ₄ Si	448.6	2.821	2.815 ^c	0.2386	-0.0073
MM	518.7	1.914	1.939 ^c	0.4190	-0.0022
MDM	564.4	1.440	1.440 ^c	0.5314	-0.0208
MD ₂ M	599.4	1.227	1.179 ^c	0.6452	-0.02486
MD ₃ M	628.4	0.945	0.996 ^c	0.7410	-0.02386
MD ₄ M	653.2	0.804	0.877 ^c	0.8210	-0.02565
MD ₅ M	671.8	0.677	0.763 ^c	0.9338	-0.04980
MD ₆ M	688.9	0.624	0.677 ^c	1.0171	-0.03970
D ₃	554.2	1.663/1.738 ^a	1.788 ^c	0.5037	-0.00419
D ₄	586.8	1.332	1.344 ^c	0.5833	-0.04690
D ₅	619.2	1.076/1.137 ^a	1.164 ^c	0.6541	-0.02718
D ₆	645.8 ^b	0.917/0.973 ^a	0.961 ^c	0.7328	-0.02190
D ₇	669.5 ^b	0.794/0.844 ^a	0.815 ^c	0.7992	-0.02615
D ₈	689.2 ^b	0.702/0.749 ^a	0.691 ^c	0.8692	-0.04738
D ₉	705.8 ^b	0.629/0.672 ^a	0.633 ^c	0.9483	-0.04282
TM ₃	596.9	1.142/1.105 ^a	1.182 ^c	0.6267	-0.02281
QM ₄	623.2	0.950/0.965 ^a	1.022 ^c	0.6873	-0.01532

^aThese values were estimated by the Lyderson/Eduljee methods. ^bThese values were estimated from the T_b/T_c vs. bp curve. ^cThese values were calculated by the Halm-Stiel correlation program.

tures of TM₃ and QM₄ are not shown. They are very close to those of MD₂M and MD₃M, respectively, and the critical points are very close to those of the linear compounds as well.

The constants for calculation of vapor pressure by the Halm-Stiel equation are given in Table XX. Since this calculation is not easily done without a computer, regressions of vapor pressure to the AIChE DIPPR equation were also done. This equation is

$$\ln(P_v) = A + B/T + C \ln(T) + DT^E \quad (4)$$

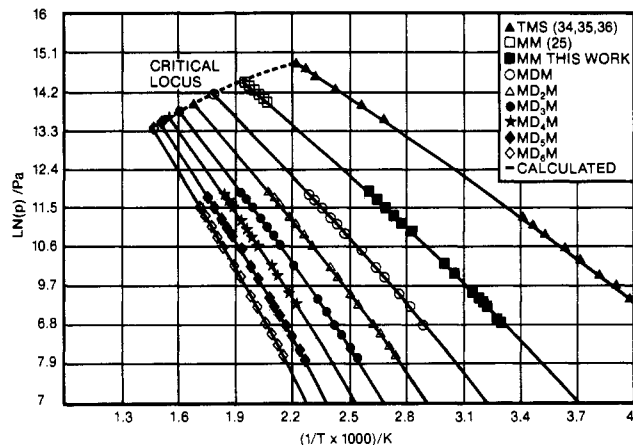
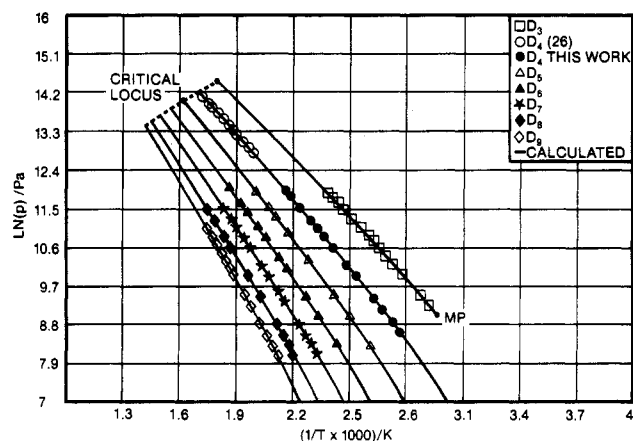
where P_v is the vapor pressure (Pa), T is the temperature (K), and A , B , C , D and E are constants. To convert from pascals to Torr (mmHg) multiply by 7.500615×10^{-3} .

These regressions were made by using the Halm-Stiel equation to calculate 50 equally spaced vapor pressure values over the range of $T_r = 0.44$ to T_c . These values were then used to calculate the DIPPR equation constants. These constants are given in Table XXI. Although the coefficient D appears very small, regression of the data without the fourth term of the equation gives much greater errors. The terms of the equation are very similar with others in the DIPPR com-

Table XXI. Vapor Pressure of Poly(dimethylsiloxanes). Constants for the AIChE DIPPR Equation^a

compd	A	B	C	D	E	RMS % error	temp range, K
Me ₄ Si	54.585	-4506.0	-4.9231	2.05190×10^{-14}	5	0.225	197-448
MM	65.614	-6315.7	-6.2846	1.71700×10^{-17}	6	0.497	228-518
MDM	81.498	-8159.9	-8.4039	1.18771×10^{-17}	6	0.923	248-564
MD ₂ M	92.559	-9700.4	-9.8210	8.98010×10^{-18}	6	1.270	263-599
MD ₃ M	100.39	-10974	-10.796	7.12285×10^{-18}	6	1.518	276-628
MD ₄ M	107.95	-12172	-11.740	5.92506×10^{-18}	6	1.753	287-653
MD ₅ M	126.19	-14199	-14.137	5.61791×10^{-18}	6	2.327	295-671
MD ₆ M	129.73	-15077	-14.530	4.90889×10^{-18}	6	2.430	303-688
D ₃	73.510	-7439.5	-7.2884	1.23355×10^{-17}	6	0.713	338-554
D ₄	95.191	-9504.6	-10.246	1.04739×10^{-17}	6	1.358	280-586
D ₅	94.421	-10153	-10.031	7.47649×10^{-18}	6	1.317	274-619
D ₆	99.273	-11155	-10.612	5.98668×10^{-18}	6	1.476	284-645
D ₇	106.53	-12288	-11.531	5.05819×10^{-18}	6	1.699	294-669
D ₈	120.19	-13888	-13.327	4.64516×10^{-18}	6	2.125	303-689
D ₉	125.39	-14865	-13.948	4.13902×10^{-18}	6	2.283	310-705
TM ₃	88.148	-9347.6	-9.2127	8.27700×10^{-18}	6	1.766	269-596
QM ₄	107.70	-11032	-11.933	1.10550×10^{-17}	6	0.992	288-623

^a $\ln(P_v) = A + B/T + C \ln(T) + DT^E$, P_v in pascal, T in kelvin.

**Figure 3. Vapor pressures of tetramethylsilane and the linear dimethylsiloxanes.****Figure 4. Vapor pressures of the cyclic dimethylsiloxanes.**

pilation (41). The root-mean-square error for these equations is larger than that found in the Halm-Stiel equation regression. They are given here only for purposes of extrapolation using a simpler equation than the Halm-Stiel. Within the range of experimental data, the Antoine equation is more accurate.

Copies of the computer programs used to calculate the Halm-Stiel equation constants and vapor pressures are available from the author.

Acknowledgment

We thank Miss Q. Weary, Mr. D. Filsinger, Mr. K. Hughes, and Mr. B. Brady for performing many of the vapor pressure measurements and Mr. T. Lane for providing the samples of D₆ and D₉.

Registry No. MM, 107-46-0; MDM, 107-51-7; MD₂M, 141-62-8; MD₃M, 141-63-9; MD₄M, 107-52-8; MD₅M, 541-01-5; MD₆M, 556-69-4; D₃, 541-05-9; D₄, 556-67-2; D₅, 541-02-8; D₆, 540-97-6; D₇, 107-50-8; D₈, 556-68-3; D₉, 556-71-8; TM₃, 17928-28-8; QM₄, 3555-47-3.

Literature Cited

- Wilcock, D. F. *J. Am. Chem. Soc.* **1946**, *68*, 691.
- Stull, D. R. *Ind. Eng. Chem.* **1947**, *39*, 517.
- Scott, D. W.; Messerly, J. F.; Guthrie, G. B.; Hossenlopp, I. A.; Moore, R. J.; Osborne, A.; Berg, W. T.; McCullough, J. P. *J. Phys. Chem.* **1961**, *65*, 1320.
- Reuther, H.; Reichel, G. *Chem. Tech. (Berlin)* **1954**, *6*, 474.
- Studenberg, J., Dow Corning, Midland, MI, 1958, unpublished data.
- Klejnot, O. J. *Inorg. Chem.* **1963**, *2*, 825.
- Skorokhodov, I. I.; Ditsent, V. E.; Terenteva, N. A.; Zolotareva, M. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1971**, *45*, 902.
- Guzman, J. A.; Kay, W. B. *Fluid Phase Equilib.* **1981**, *7*, 187.
- Hunter, M. J.; Hyde, J. F.; Warrick, E. L.; Fletcher, H. J. *J. Am. Chem. Soc.* **1946**, *68*, 667.
- Hunter, M. J.; Warrick, E. L.; Hyde, J. F.; Currie, C. C. *J. Am. Chem. Soc.* **1946**, *68*, 2294.
- Othmer, D. F. *Ind. Eng. Chem.* **1957**, *49*, 125.
- Marchand, M. *Chem. Tech. (Berlin)* **1952**, *4*, 111.
- Potashova, G. A.; Kleinovskaya, M. A.; Molokanova, Yu. K.; Ditsent, V. E.; Skorokhodov, I. I. *Russ. J. Phys. Chem. (Engl. Transl.)* **1976**, *50*, 665.
- Osthoff, R. C.; Grubb, W. T.; Burkhard, C. A. *J. Am. Chem. Soc.* **1953**, *75*, 2227.
- Osthoff, R. C.; Grubb, W. T. *J. Am. Chem. Soc.* **1954**, *76*, 399.
- Ditsent, V. E.; Skorokhodov, I. I.; Terenteva, N. A.; Zolotareva, M. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1971**, *45*, 901.

- Bragin, G. P.; Karapetyants, M. K. *Russ. J. Phys. Chem. (Engl. Transl.)* **1974**, *48*, 612.
- Lopatkina, I. L.; Kucherskaya, L. B.; Kuznetsova, A. G.; Shaulov, Yu. K. *Russ. J. Phys. Chem. (Engl. Transl.)* **1973**, *47*, 1626.
- Stull, D. R. *Ind. Eng. Chem. Anal. Ed.* **1946**, *18*, 234.
- Osborne, N. S.; Meyers, C. H. *J. Res. Natl. Bur. Stand.* **1934**, *13*, 1.
- Willingham, C. B.; Taylor, W. J.; Pignocco, J. M.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 219.
- Dean, J. D., Ed. *Langes's Handbook of Chemistry*, 6th ed.; McGraw-Hill: New York, 1979.
- Halm, R. L.; Stiel, L. I. *AIChE J.* **1967**, *13*, 351.
- Pitzer, K. S.; Lippman, D. S.; Curl, R. F.; Huggins, C. M.; Peterson, D. E. *J. Am. Chem. Soc.* **1955**, *77*, 3433.
- McLure, I. A.; Dickinson, E. J. *Chem. Thermodyn.* **1976**, *8*, 93.
- Young, C. L. *J. Chem. Thermodyn.* **1972**, *4*, 65.
- Pollnow, G. P. Dow Corning, Midland, MI, 1957, unpublished data.
- Cholpan, P. P. *Ukr. Fiz. Zh.* **1964**, *9*, 1016.
- Young, C. L. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 452.
- Young, C. L. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 580.
- Hicks, C. P.; Young, C. L. *J. Chem. Soc., Faraday Trans. 1* **1971**, *72*, 122.
- Dickinson, E.; McLure, I. A. *J. Chem. Soc., Faraday Trans. 1* **1972**, *70*, 2313.
- McLure, I. A.; Neville, J. F. *J. Chem. Thermodyn.* **1977**, *9*, 957.
- McGlashan, M. L.; McKinnon, I. P. *J. Chem. Thermodyn.* **1979**, *9*, 1205.
- Aston, J. G.; Kennedy, R. M.; Messerly, G. H. *J. Am. Chem. Soc.* **1941**, *63*, 2243.
- Hicks, C. P.; Young, C. L. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 122.
- Lyderson, A. L. *Eng. Exp. Stn. Report 3*. University of Wisconsin: Madison, WI, 1955.
- Reid, R. C.; Prausnitz, J. M.; Sherwood, J. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1973.
- Gambill, W. R. *Chem. Eng.* **1959**, *66*(12), 181.
- Gambill, W. R. *Chem. Eng.* **1959**, *66*(14), 157.
- Danner, R. P.; Daubert, J. E., Eds. *AIChE, DIPPR Data Compilation*, New York, 1985.

Received for review June 27, 1985. Revised manuscript received December 26, 1985. Accepted January 27, 1986.

Density of Deuterated Isobutyric Acid between 11 and 30 °C

Sandra C. Greer

Department of Chemistry and Biochemistry, The University of Maryland, College Park, Maryland 20742

The density of 94%-deuterated isobutyric acid has been measured between 11 and 30 °C with an uncertainty of 3×10^{-5} g/cm³. The density as a function of temperature can be represented by the equation d_{94} (g/cm³) = $1.060866 - 0.001117t + 1.4 \times 10^{-7}t^2$, where the temperature, t , is in degrees Celsius. The density of fully deuterated isobutyric acid is calculated to be d_{100} (g/cm³) = $d_{94} + 0.0056$ (± 0.003).

I. Introduction

The density of 94%-deuterated isobutyric acid has been measured between 11 and 30 °C by means of a magnetic suspension densimeter with a calibration accuracy of 3×10^{-5} g/cm³ and a precision of 5×10^{-6} . There have been no previous reports of the density of deuterated isobutyric acid.

II. Experimental Methods

A. Sample Material. Isobutyric acid in which the hydrogen atoms (paraffinic as well as acidic) had been replaced by deuterium atoms was obtained from Merck, Sharp, and Dohme Canada, Ltd. The material was specified to be 98% deuterated, but mass spectrometric analysis indicated a deuteration of 94.1% \pm 0.3%. The material was handled in a dry nitrogen atmosphere.

Table I. Density of 94%-Deuterated Isobutyric Acid as a Function of Temperature

temp, °C	density, g/cm ³	temp, °C	density, g/cm ³
11.393	1.048 160	25.792	1.032 159
16.918	1.042 010	30.077	1.027 400
21.472	1.036 943	30.459	1.026 972

B. Temperature Control and Measurement. The temperature of the sample was controlled to 0.001 °C by circulating water. The temperature was measured by a quartz thermometer which had been calibrated with respect to a platinum resistance thermometer on the International Practical Temperature Scale of 1968. Temperatures are thus accurate to 0.002 °C.

C. Density Measurement. The density of the deuterated isobutyric acid was measured by means of a magnetic suspension densimeter (1, 2). In this instrument, a small quartz buoy containing a magnet is levitated in the sample by means of a solenoid and a feedback system. The square of the solenoid current required to support the buoy in the liquid sample is linearly related to the fluid density. The instrument was calibrated by suspending the buoy in liquids of known density. In this case, solutions of sucrose in water were used (3). The calibration had an uncertainty of 3×10^{-5} g/cm³, which would usually determine the accuracy of the measurements. For deuterated isobutyric acid, however, the lower limit on the accuracy was determined by the uncertainty in the extent of