Orthobaric Liquid Densities for Octamethylcyclotetrasiloxane, Decamethylcyclopentasiloxane, Dimethicone 20, and a Cyclic Poly(dimethylsiloxane)

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The orthobaric liquid-state densities of octamethylcyclotetrasiloxane (292–408 K), decamethylcyclopentasiloxane (302–451 K), and two dimethylsiloxane polymers—one a linear polymer of molecular weight around 1900 (292–470 K) and the other a closely-fractionated cyclic polymer of molecular weight 2935 (302–455 K)—have been determined using a hydrostatic density balance over the temperature ranged quoted. The resulting specific volumes have been fitted to a simple quartic power series in temperature.

Introduction

With a view chiefly to exploring the applicability to cyclic dimethylsiloxane oligomers and polymers of a phenomenological principle of corresponding states shown previously (*1*) to be applicable to short-chain dimethylsiloxane oligomers, we have determined by a hydrostatic density balance the orthobaric densities of octamethylcyclotetrasiloxane from 292 to 406 K, decamethylcyclopentasiloxane from 302 to 451 K, and a cyclic dimethylsiloxane polymer of molecular weight 2935 from 302 to 455 K. To extend the comparison with linear dimethylsiloxane polymers, we have also determined the orthobaric density of a linear dimethylsiloxane polymer of molecular weight 1900 from 292 to 470 K.

Experimental Section

The octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane were obtained by careful vacuum fractionation using a Nester Faust spinning-band distillation column from a sample of XF 218 fluid kindly supplied by Dow Corning Ltd. and purified by Dr. J. F. Neville at their Barry laboratory. Their purities were determined to be in excess of 99.5 mol % by GLC using a Carlo Erba research chromatograph (model 4200) fitted with a 1.8-m × 4-mm-i.d. FFAP on Diatomite CLQ (80-100 mesh) packed column. Detection was by flame ionization, and N_2 was used as the carrier gas. The linear poly(dimethylsiloxane) was obtained from Dow Corning dimethicone 20, batch 995580. The cyclic poly(dimethylsiloxane) was kindly supplied to Drs. J. A. Semlyen and S. Clarson of the University of York. It was characterized by analytical gel permeation chromatography. The number average of skeletal bonds n_n, the molecular weight M_n, and the heterogeneity index M_w/M_n were reported to be 79, 2935, and 1.03, respectively. All the materials were dried over anhydrous calcium chloride and exhaustively degassed before their densities were determined.

Table I. Orthobaric Specific Volumes *v* of Octamethylcyclotetrasiloxane at Temperatures *T*: (a) Measured and (b) Calculated from Fitted Coefficients[a]

	$v/(\mathrm{cm^3 \cdot g^{-1}})$			$v/(\mathrm{cm^3 \cdot g^{-1}})$	
T/K	a	b	T/K	a	b
292.055	1.044 24	1.044 27	351.376	1.124 54	1.124 55
297.501	1.051 14	1.051 09	360.327	1.138 08	1.138 09
305.450	1.061 19	1.061 21	370.810	1.154 58	1.154 55
315.054	1.073 70	1.073 72	381.046	1.171 30	1.171 31
324.321	1.086 14	1.086 13	392.205	1.190 38	1.190 40
333.836	1.099 25	1.099 25	402.677	1.209 22	1.209 20
342.330	1.111 32	1.111 31	408.218	1.219 51	1.219 51

[a] $\ln(v/(\mathrm{cm^3 \cdot g^{-1}})) = -0.366\,54 + 2.0268 \times 10^{-3}(T/\mathrm{K}) - 3.5429 \times 10^{-6}(T/\mathrm{K})^2 + 4.8217 \times 10^{-9}(T/\mathrm{K})^8$. $\sigma = 0.2 \times 10^{-4}\ \mathrm{cm^3 \cdot g^{-1}}$.

Table II. Orthobaric Specific Volumes *v* of Decamethylcyclopentasiloxane at Temperatures *T*: (a) Meausred and (b) Calculated from Fitted Coefficeints[a]

	$v/(\mathrm{cm^3 \cdot g^{-1}})$			$v/(\mathrm{cm^3 \cdot g^{-1}})$	
T/K	a	b	T/K	a	b
302.193	1.054 05	1.054 10	380.396	1.155 95	1.155 81
311.530	1.065 22	1.065 19	391.613	1.172 63	1.172 58
320.280	1.075 93	1.075 79	403.105	1.190 52	1.190 52
329.424	1.087 04	1.087 09	414.779	1.209 57	1.209 61
338.827	1.098 92	1.098 99	426.652	1.229 94	1.230 01
348.981	1.112 15	1.112 20	439.326	1.253 01	1.252 99
358.448	1.124 81	1.124 88	451.360	1.276 09	1.276 07
369.195	1.139 77	1.139 74			

[a] $\ln(v/(\mathrm{cm^3 \cdot g^{-1}})) = -0.369\,19 + 2.0856 \times 10^{-3}(T/\mathrm{K}) - 3.6389 \times 10^{-6}(T/\mathrm{K})^2 + 4.4910 \times 10^{-9}(T/\mathrm{K})^3$. $\sigma = 0.6 \times 10^{-4}\ \mathrm{cm^3 \cdot g^{-1}}$.

The experimental measurements of density were carried out in an apparatus, previously located in the National Physical Laboratory at Teddington, whose distinguishing feature is a magnetically levitated Archimedian bob. The two-phase fluid sample is kept in a sealed borosilicate glass cell. An iron core enclosed in a silica envelope, known collectively as the bob, is levitated in the midst of the fluid by means of an electronically-controlled induced magnetic field. The measured apparent change of weight of the cell on levitation and the known volume of the bob lead to the calculation of the density of the fluid where the bob is situated. Different cells are available for measurements in the liquid or the vapor phases (*2*).

During the experimental run, the cell hangs from the pan of an automatic balance through a 0.125-mm-o.d. steel suspension wire and is kept inside a block thermostat useable up to at least 650 K. The block includes heaters, a platinum control element, and two platinum resistance thermometers. A sensitive proportional controller holds the block temperature within about ±0.005 K over the 1-h measurement period. Finally, a platinum resistance thermometer is attached close to the cell wall for temperature measurement of the fluid sample. Full details of the apparatus and variations in approach used in this particular investigation are available (*3*).

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Table III. Orthobaric Specific Volumes *v* of Dimethicone 20 at Temperatures *T*: (a) Measured and (b) Calculated from Fitted Coefficients[a]

	$\upsilon/(\mathrm{cm^3 \cdot g^{-1}})$			$\upsilon/(\mathrm{cm^3 \cdot g^{-1}})$	
T/K	a	b	*T*/K	a	b
292.378	1.048 83	1.048 76	375.948	1.137 12	1.137 09
296.889	1.053 30	1.053 32	385.988	1.148 45	1.148 40
298.654	1.055 02	1.055 11	396.109	1.159 93	1.159 99
306.545	1.063 13	1.063 14	406.718	1.172 30	1.172 37
314.348	1.071 21	1.071 15	417.497	1.185 28	1.185 20
322.392	1.079 48	1.079 48	428.277	1.198 34	1.198 29
330.765	1.088 26	1.088 22	438.548	1.211 00	1.211 03
339.212	1.097 13	1.097 13	449.462	1.224 83	1.224 87
348.015	1.106 44	1.106 52	459.848	1.238 34	1.238 35
357.087	1.116 32	1.116 32	470.531	1.252 57	1.252 55
366.059	1.126 14	1.126 13			

[a] $\ln(\upsilon/(\mathrm{cm^3 \cdot g^{-1}})) = -0.270\,77 + 1.3305 \times 10^{-3}(T/\mathrm{K}) - 1.2181 \times 10^{-6}(T/\mathrm{K})^2 + 1.3398 \times 10^{-9}(T/\mathrm{K})^8$. $\sigma = 0.5 \times 10^{-4}$ $\mathrm{cm^3 \cdot g^{-1}}$.

Table IV. Orthobaric Specific Volumes *v* of a Cyclic Dimethylsiloxane Polymer at Temperatures *T*: (a) Measured and (b) Calculated from Fitted Coefficients[a]

	$\upsilon/(\mathrm{cm^3 \cdot g^{-1}})$			$\upsilon/(\mathrm{cm^3 \cdot g^{-1}})$	
T/K	a	b	*T*/K	a	b
302.260	1.033 52	1.033 55	380.507	1.111 07	1.111 03
307.290	1.038 41	1.038 35	391.338	1.122 36	1.122 33
315.250	1.046 01	1.046 00	402.106	1.133 74	1.133 73
323.273	1.053 76	1.053 76	413.152	1.145 64	1.145 62
331.687	1.061 94	1.061 96	424.420	1.157 89	1.157 96
340.042	1.070 11	1.070 17	435.761	1.170 63	1.170 62
349.085	1.079 15	1.079 13	446.652	1.182 92	1.183 00
359.843	1.089 90	1.089 92	455.143	1.192 91	1.192 83
370.164	1.100 38	1.100 39			

[a] $\ln(\upsilon/(\mathrm{cm^3 \cdot g^{-1}})) = -0.282\,03 + 1.2614 \times 10^{-3}(T/\mathrm{K}) - 1.0535 \times 10^{-6}(T/\mathrm{K})^2 + 1.0872 \times 10^{-9}(T/\mathrm{K})^3$. $\sigma = 0.4 \times 10^{-4}$ $\mathrm{cm^3 \cdot g^{-1}}$.

Results

The results of the determination of density are presented in Tables I–IV in terms of the specific volume υ as a function of temperature T in the IPTS-68 scale.

For convenience in obtaining thermal expansion coefficients by direct differentiation, the results of the measurements were fitted to expressions of the form $\ln(\upsilon/(\mathrm{cm^3 \cdot g^{-1}})) = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 + d(T/\mathrm{K}).^3$. The least-squares fitted coefficients are also listed in Table I–IV. In every case the reported standard deviation is well within the experimental error of no more than 0.000 06 $\mathrm{cm^3 \cdot g^{-1}}$.

Discussion

Other results that we have been able to find in the literature extending over a reasonable range of temperatures are those of Hurd (*4*) for both octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane from 273 to 353 K. The calculated values of specific volumes by using the coefficients reported in Tables I and II, at the four temperature points in which there is an overlapping of experimental measurements, are in good agreement to within 0.1% for both substances.

Much later Marsh (*5*) reported the densities of octamethylcyclotetrasiloxane in the temperature range form 298.15 to 333.15 K. We used both his equation and fitted coefficients in order to compare the calculated values of specific volume for four of our experimental measurements in the overlapping temperature range. There is excellent agreement to within 0.035% between the results of these two works.

Registry Numbers Supplied by Author. Octamethylcyclotetrasiloxane, 293-51-6; decamethylcyclopentasiloxane, 294-40-6.

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