Temperature-Dependent Vapor Pressure of Selected Cyclic and Linear Polydimethylsiloxane Oligomers

Ying Duan Lei,[†,‡,§] Frank Wania,*[,§] and Dan Mathers[‡]

Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, Canada, M5S 3E5, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6, and Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada, M1C 1A4

The isothermal retention times of seven cyclic (D_4 to D_{10}) and nine linear (L_5 to L_{13}) dimethylsiloxane oligomers on a nonpolar gas chromatographic column were determined at temperatures between (308.15 and 438.15) K. Using normal alkanes as standard reference and calibration compounds, these retention times were used to derive liquid state vapor pressures at 298.15 K as well as enthalpies of vaporization that allow for the estimation of vapor pressures over a wide range of temperatures. The data agree within 0.25 log units with vapor pressure values previously reported by Flaningam (1986) but extend those values to lower temperatures and larger oligomers. Cyclic dimethylsiloxanes are more volatile than linear dimethylsiloxanes of a similar size. Oligomers with 10 and more dimethylsiloxane units are expected to sorb appreciably to aerosol at environmentally relevant temperatures.

Introduction

Siloxanes are compounds with a backbone consisting of alternating silicon and oxygen atoms (−Si−O−Si−O−), with organic side chains attached to the silicon atoms. In dimethylsiloxanes the side chains are methyl groups. They exist both in linear and cyclic forms, and different oligomers vary in the number of $-Si(CH_3)_2-O-$ units. Linear dimethylsiloxanes are referred to as L_X, where X refers to the number of $-Si(CH_3)_2-O-$ units. For example, L_5 is dodecamethylpentasiloxane, and L_{13} is octacosamethyltridecasiloxane. Similarly, cyclic dimethylsiloxanes are referred to as D_X, D_5 designating decamethylcyclopentasiloxane, and D_{10} is eicosamethylcyclodecasiloxane.

The dimethylsiloxane oligomers have a wide range of applications worldwide. In particular, they are common constituents of personal care products, paints, varnishes, lacquers, and furniture polishes.[1] Long-chain linear dimethylsiloxane oligomers are also used in transformer dielectric and heat transfer components.[2] Dimethylsiloxane oligomers are released into the environment either via direct evaporation from products or via wastewater and sewage treatment plants.[3,4] D_5, one of the more volatile oligomers used in large quantities, has been detected in the atmosphere at levels consistent with the used quantities.[5]

It is essential to have reliable physical-chemical property data of the dimethylsiloxane oligomers to understand and quantify their environmental fate. Data have been reported for their partitioning between water and air[6−8] and between water and organic matter.[9,10] In particular, a measure of volatility such as vapor pressure is required to quantify rates of volatilization from products containing dimethylsiloxane oligomers, from soils,[11] from water, and from sewage treatment plants[3,4] or to describe the chemical partitioning between the gas phase and the particles in both the atmosphere and the indoor environment.[2] Also, when choosing sorbents for air sampling, the vapor pressure can aid in estimating breakthrough behavior.[12] Quantitative understanding of the temperature dependence of the vapor pressure within the environmental temperature range is desirable.

Flaningam[13] has previously reported vapor pressures for several dimethylsiloxane oligomers. There is nevertheless need for additional measurements, because the ebuliometric technique used by Flaningam[13] is limited to measuring vapor pressures in excess of 3000 Pa. The available experimental data are thus restricted to relatively small oligomers (L_5 to L_8 and D_4 to D_9), and relatively high temperatures. The lowest experimental temperature ranged from 361.75 K for D_4 to 473.15 K for D_9.[13] Extrapolation of the measured vapor pressures to larger dimethylsiloxane oligomers and lower temperatures will inevitably introduce errors of largely unknown size. In particular, efforts to reconcile data on the vapor pressure, water solubility and Henry's law constants of the smaller dimethylsiloxane oligomers have not always been successful,[8] suggesting a need to confirm the vapor pressure data by Flaningam.[13]

The gas chromatographic retention time (GCRT) technique by Bidleman[14] is well-suited for the determination of the liquid state vapor pressure of a low volatility compound. In particular, it is applicable to nonpolar compounds such as the dimethylsiloxane oligomers, because gas chromatographic columns with a nonpolar stationary phase that has partitioning properties that resemble closely those of the pure liquid substance are readily available. Also, normal alkanes of variable chain length, which have exceptionally well-established vapor pressures can serve as reliable reference and calibration compounds for nonpolar organic substances. Finally, the GCRT technique does not

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[*] To whom correspondence should be addressed. E-mail address: frank.wania@utoronto.ca.
[†] Department of Chemical Engineering and Applied Chemistry, University of Toronto.
[‡] Department of Chemistry, University of Toronto.
[§] Department of Physical and Environmental Sciences, University of Toronto Scarborough.

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require the availability of pure substances, which is important as many dimethylsiloxane oligomers are only available as mixtures.

In this paper, we report the temperature-dependent liquid state vapor pressure for seven cyclic (D_4 to D_{10}) and nine linear (L_5 to L_{13}) dimethylsiloxane oligomers, which were determined by the GCRT method[14] at temperatures considerably lower than those employed by Flaningam.[13] Normal alkanes were used as standard reference and calibration compounds. Furthermore, we compared the new data with those reported by Flaningam[13] and others and estimated the fraction of these compounds adsorbed to aerosol as a function of temperature.

Experimental Section

Chemicals. Mixtures of dimethylsiloxane oligomers were obtained from Dow Corning Corporation (Midland, MI). Normal C_{10} to C_{20} alkanes were obtained from Aldrich (Oakville, Ontario, Canada). The stock solutions of the chemicals were prepared by dissolving a small amount of chemical into high-performance liquid chromatography (HPLC) grade hexane (Caledon Laboratories, Ontario, Canada). Then the stock solutions were further diluted with hexane.

Instrumentation. Isothermal retention time of the target compounds at five to eleven temperatures in the range (308.15 to 438.15) K were determined using a Perkin-Elmer XL gas chromatograph equipped with a flame ionization detector and a DB-1 capillary column (0.25 mm inner diameter × 1.0 m long, 0.25 μm film thickness, J&W Scientific, Folsom, CA). Temperatures of the injection port and detector were (498.15 and 523.15) K, respectively. Hydrogen was used as a carrier at 3.45 kPa. The split ratio was 25:1.

Data Analysis. The method employed here has been used and described previously[14,15] and will not be described in detail again. Briefly, the logarithm of the ratios of the measured isothermal GCRTs of the target analyte (t_R) and a standard reference compound ($t_{R,ref}$) at each temperature (T) are linearly regressed against the logarithm of the vapor pressure ($P_{L,ref}$) of the reference compound at that temperature:

$$\ln(t_R(T)/t_{R,ref}(T)) = [1 - (\Delta_{vap}H/\Delta_{vap}H_{ref})]\ln(P_{L,ref}(T)/\mathrm{Pa}) - C \quad (1)$$

The slope and intercept of these regressions give the ratio of the enthalpies for target analyte and standard reference compound ($\Delta_{vap}H/\Delta_{vap}H_{ref}$) and the constant C, which are then used to calculate a vapor pressure P_{GC} at 298.15 K using:

$$\ln(P_{GC}(298.15\ \mathrm{K})/\mathrm{Pa})) = (\Delta_{vap}H/\Delta_{vap}H_{ref})\ln(P_{L,ref}(298.15\ \mathrm{K})/\mathrm{Pa}) + C \quad (2)$$

P_{GC} is not always identical to the vapor pressure of the (supercooled) liquid P_L, necessitating a calibration with closely related compounds. Because the enthalpy of vaporization of the standard reference compound $\Delta_{vap}H_{ref}$ is known, the enthalpy of vaporization can be obtained from the ratio ($\Delta_{vap}H/\Delta_{vap}H_{ref}$).

The method thus requires two types of substances with known vapor pressure: to determine P_{GC} values, a standard reference compound whose vapor pressure is very well-known as a function of temperature is required. To convert these P_{GC} values into P_L values, we need a number of calibration compounds whose vapor pressure at 298.15 K is well-known. Ideally, the reference and calibration compounds are structurally similar to the substances for which vapor pressure is to be determined, because then it is more likely that their interaction with the GC column's stationary phase can be used to represent the tendency to evaporate from their liquid phase. Because no reliable vapor pressure data for organosiloxane compounds in the temperature range of the retention time measurements were available, one of three normal alkanes was used as the standard reference compound, and several other normal alkanes were used as calibration compounds. Previous studies relying on the GCRT technique[14] have succeeded, despite the use of calibration compounds that were not structurally similar to the solutes of interest, as long as both are relatively nonpolar.

Vapor Pressures and Enthalpies of Vaporization for the Standard Reference Compounds. The GCRT method relies on standard reference compounds whose liquid state vapor pressure is known very accurately within the temperature range of the retention time measurements.[14] Three normal alkanes (tridecane, pentadecane, octadecane) were used as standard reference compounds. More than one reference compound was necessary because of coelution of peaks and also because the volatility of target analytes and standard reference compounds should not be too different. C_{13} was used for D_4 and D_5, C_{18} for D_6 to D_{10}, and C_{15} for all linear siloxanes (L_5 to L_{13}). Liquid state vapor pressures (P_L) of the three alkanes were compiled from the literature[16−21] and regressed against the reciprocal absolute temperature within the temperature range of the retention time measurements yielding the following equations:

tridecane (298.15 to 368.15) K:

$$\log(P_L/\mathrm{Pa}) = 11.83 - 3290.5(T/\mathrm{K})^{-1} \quad (3)$$
$$r^2 = 0.9997$$

pentadecane (298.15 to 438.15) K:

$$\log(P_L/\mathrm{Pa}) = 11.884 - 3598.5(T/\mathrm{K})^{-1} \quad (4)$$
$$r^2 = 0.9985$$

octadecane (298.15 to 383.15) K:

$$\log(P_L/\mathrm{Pa}) = 13.227 - 4419(T/\mathrm{K})^{-1} \quad (5)$$
$$r^2 = 0.9999$$

The very high r^2 values attest to the strong linearity of the relationships between the logarithm of the liquid state vapor pressure and reciprocal temperature over the temperature range of the retention time measurements.

Vapor Pressures of the Calibration Compounds. The vapor pressure values obtained directly from the GCRTs (eq 2), called P_{GC}, need to be calibrated against P_L values obtained by other means.[14] Eight or nine normal alkanes (C_{10} to C_{20}) were used to establish calibration curves (Figure 1). The P_{GC} values for these alkanes as determined by the GCRT method were regressed against the vapor pressure of the supercooled liquid P_L at 298.15 K as recommended in Mackay et al.[22] The P_{GC} values are slightly different depending on which alkane served as a standard reference compound. Accordingly, three different calibration curves were derived (Figure 1):

C_{13} as the reference compound:

$$\log(P_L/\mathrm{Pa}) = (1.0354 \pm 0.0131)\log(P_{GC}/\mathrm{Pa}) - (0.0578 \pm 0.00207) \quad (6)$$
$$r^2 = 0.999,\ n = 9$$

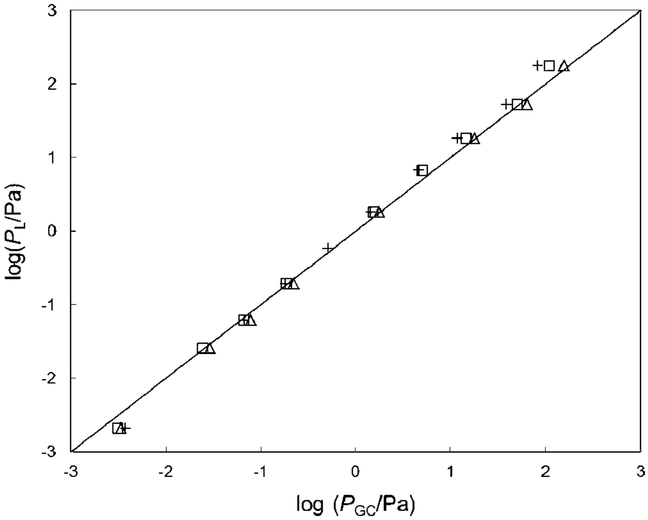

Figure 1. Relationship between the P_{GC} derived from GCRTs and the literature-reported P_L for normal alkanes with 10 to 20 carbon atoms, which is used to calibrate the method used to determine P_L for dimethylsiloxane oligomers. P_{GC} values are slight different depending on whether △, tridecane; □, pentadecane; or +, octadecane is used as a standard reference compound.

C_{15} as the reference compound:

$$\log(P_L/\text{Pa}) = (1.056 \pm 0.015)\log(P_{GC}/\text{Pa}) + (0.0371 \pm 0.0218) \quad r^2 = 0.9985,\ n = 8 \tag{7}$$

C_{18} as the reference compound:

$$\log(P_L/\text{Pa}) = (1.1102 \pm 0.0139)\log(P_{GC}/\text{Pa}) + (0.0638 \pm 0.0184) \quad r^2 = 0.9989,\ n = 9 \tag{8}$$

Results

Table 1 lists the measured and calibrated vapor pressures P_{GC} and P_L at 298.15 K, as well as the enthalpies of vaporization $\Delta_{vap}H$ of the 16 dimethylsiloxane oligomers applicable to the temperature range of the retention time measurements. The P_{GC} values for the calibration compounds are given in the Supporting Information. For the easy calculation of P_L as a function of temperature, Table 1 also lists intercepts b_L and slopes m_L of the temperature regressions:

$$\log(P_L/\text{Pa}) = m_L/(T/\text{K}) + b_L \tag{9}$$

m_L and b_L were obtained from P_L at 298.15 K and $\Delta_{vap}H$. The precision of the P values is very high because of the high reproducibility of GCRT measurements. The actually measured retention times are given in several tables in the Supporting Information. The uncertainty of the enthalpy of vaporization and the regression parameters m_L and b_L is not quantified, because it depends almost entirely on the precision of the enthalpy of vaporization of the standard reference compounds $\Delta_{vap}H_{ref}$.

Discussion

Comparison of the P_L Values of Dimethylsiloxane Oligomers with Literature Values. Figure 2 compares the vapor pressures of the pure liquid for D4 and D5 from this study with those reported by Marsh,[23] Young,[24] Flaningam,[13] and Palczewska-Tulinska and Oracz.[25] The agreement for D5 is excellent, in particular between our data and those by Palczewska-Tulinska and Oracz,[25] which overlap in the temperature range (348 to 370) K. Our vapor pressure value for D4 at 308.15 K is within 0.06 log units of that reported by Marsh.[23] At higher temperatures around 363.15 K, the new data are approximately 0.15 log units lower than those reported by Flaningam[13] and Palczewska-Tulinska and Oracz.[25]

For dimethylsiloxane oligomers other than D4 and D5, only Flaningam[13] has reported vapor pressure values. In Figures 3 and 4 the log(P_L/Pa) values from this study and those reported by Flaningam[13] are plotted against the reciprocal absolute temperature. Generally, the Flaningam measurements cover a higher temperature range than the data reported here.[13] Other than for D4, the two studies only report vapor pressure values for D_6 and L_5 within the same temperature range, and a direct comparison is possible. The vapor pressures for D_6 at around 413.15 K are again within 0.15 log units of each other. The P_L values of L_5 in the temperature range (393.15 to 403.15) K reported by the two studies are within 0.25 log units. Overall, this indicates a very good agreement considering the widely divergent approaches employed by the two studies. Also visually the two studies are in excellent agreement, both with respect to the difference in P_L of compounds differing by one dimethylsiloxane unit (the distance between the data for different compounds in Figures 3 and 4) and the temperature dependence (the slopes in those figures). Over the very large temperature ranges covered by both studies together, the relationships between log(P_L/Pa) versus $1/T$ are no longer linear. Both the differences between dimethylsiloxane oligomers of different size and the temperature dependence increase at lower temperatures.

Relationship between log P_L and Molecular Mass. Figures 3 and 4 indicate that the vapor pressure of the linear and cyclic oligomers decreases consistently with each additional dimethylsiloxane unit. The log P_L at 298.15 K is plotted against molecular mass M in g·mol^{-1} in Figure 5. The relationship between log P_L and M is highly linear for both cyclic siloxanes:

$$\log(P_L/\text{Pa}) = -0.0115M + 5.5098 \qquad r^2 = 0.9989 \tag{10}$$

and linear siloxanes:

$$\log(P_L/\text{Pa}) = -0.0122M + 5.3945 \qquad r^2 = 0.9998 \tag{11}$$

The slopes of these relationships imply that the vapor pressure of the cyclic and linear dimethylsiloxane oligomers at 298.15 K decreases by 0.85 and 0.90 log units for each additional $-\text{Si(CH}_3)_2-\text{O}-$ unit (74.15 g·mol^{-1}). Cyclic oligomers are slightly more volatile than the equivalent linear oligomers, but not only because they have two methyl groups less and one oxygen more and therefore are 14.07 g·mol^{-1} lighter. If that were the case, the two lines in Figure 5 would fall on top of each other. The distance between the two lines in Figure 5 indicates an additional difference in P_L between 0.38 log units (for dimethylsiloxane oligomers with five $-\text{Si(CH}_3)_2-\text{O}-$ units)

Table 1. Names, Chemical Abstracts Service Registry Numbers (CAS RNs), Standard Reference Compounds, Temperature Ranges of the Retention Time Measurements, GCRT Determined Vapor Pressures P_{GC}, Liquid State Vapor Pressures P_L at 298.15 K, Slopes m_L and Intercepts b_L for Equation 9, and Enthalpies of Vaporization $\Delta_{vap}H$ for 16 Dimethylsiloxane Oligomers

				T range	P_{GC}	P_L			$\Delta_{vap}H$
ID	compound	CAS RN	ref	K	Pa	Pa	m_L	b_L	kJ·mol^{-1}
D_4	octamethylcyclotetrasiloxane	556-67-2	C_{13}	308.15−368.15	92.8 ± 0.9	124.5 ± 6.2	−2526	10.57	−48
D_5	decamethylcyclopentasiloxane	541-02-6	C_{13}	308.15−368.15	16.2 ± 0.1	20.4 ± 1.1	−3128	11.80	−60
D_6	dodecamethylcyclohexasiloxane	540-97-6	C_{18}	338.15−418.15	$(18.2 \pm 0.9) \cdot 10^{-1}$	2.26 ± 1.44	−3380	11.69	−65
D_7	tetradecamethylcycloheptasiloxane	107-50-6	C_{18}	338.15−418.15	$(29.2 \pm 0.3) \cdot 10^{-2}$	$(3.0 \pm 0.2) \cdot 10^{-1}$	−3865	12.43	−74
D_8	hexadecamethylcyclooctasiloxane	556-68-3	C_{18}	338.15−418.15	$(47.9 \pm 0.8) \cdot 10^{-3}$	$(4.0 \pm 0.2) \cdot 10^{-2}$	−4341	13.16	−83
D_9	octadecamethylcyclononasiloxane	556-71-8	C_{18}	338.15−418.15	$(9.0 \pm 0.1) \cdot 10^{-3}$	$(6.2 \pm 0.3) \cdot 10^{-3}$	−4756	13.74	−91
D_{10}	eicosamethylcyclodecasiloxane	18772-36-6	C_{18}	358.15−418.15	$(19.0 \pm 0.3) \cdot 10^{-4}$	$(11.0 \pm 0.5) \cdot 10^{-4}$	−5113	14.19	−98
L_5	dodecamethylpentasiloxane	141-63-9	C_{15}	338.15−408.15	$(50.0 \pm 0.8) \cdot 10^{-1}$	6.0 ± 0.5	−3034	10.95	−58
L_6	tetradecamethylhexasiloxane	107-52-8	C_{15}	338.15−438.15	$(62.0 \pm 0.5) \cdot 10^{-2}$	0.66 ± 0.16	−3650	12.06	−68
L_7	hexadecamethylheptasiloxane	107-50-6	C_{15}	338.15−438.15	$(77.9 \pm 0.2) \cdot 10^{-3}$	$(7.4 \pm 0.4) \cdot 10^{-2}$	−4249	13.12	−89
L_8	octadecamethyloctasiloxane	556-69-4	C_{15}	338.15−438.15	$(11.0 \pm 0.1) \cdot 10^{-3}$	$(9.3 \pm 0.5) \cdot 10^{-3}$	−4764	13.95	−98
L_9	eicosamethylnonasiloxane	2652-13-3	C_{15}	348.15−438.15	$(16.0 \pm 0.3) \cdot 10^{-4}$	$(12.1 \pm 0.6) \cdot 10^{-4}$	−5261	14.73	−107
L_{10}	docosamethyldecasiloxane	556-70-7	C_{15}	368.15−438.15	$(21.7 \pm 0.7) \cdot 10^{-5}$	$(14.7 \pm 0.8) \cdot 10^{-5}$	−5782	15.56	−116
L_{11}	tetracosamethylundecasiloxane	107-53-9	C_{15}	378.15−438.15	$(30.4 \pm 2.4) \cdot 10^{-6}$	$(18.5 \pm 0.9) \cdot 10^{-6}$	−6288	16.36	−124
L_{12}	hexacosamethyldodecasiloxane	2471-08-1	C_{15}	388.15−438.15	$(46.9 \pm 4.6) \cdot 10^{-7}$	$(25.7 \pm 1.3) \cdot 10^{-7}$	−6753	17.06	−132
L_{13}	octacosamethyltridecasiloxane	2471-09-2	C_{15}	398.15−438.15	$(70.9 \pm 5.1) \cdot 10^{-8}$	$(34.9 \pm 1.8) \cdot 10^{-8}$	−7228	17.79	−131

and 0.64 log units (for dimethylsiloxane oligomers with 10 $-Si(CH_3)_2-O-$ units). We infer from this that the cyclical dimethylsiloxane oligomers are slightly less able to interact with each other by van der Waals forces than the linear dimethylsiloxane oligomers and that this difference in the ability of cyclic and linear molecules to interact with each other increases with the chain length.

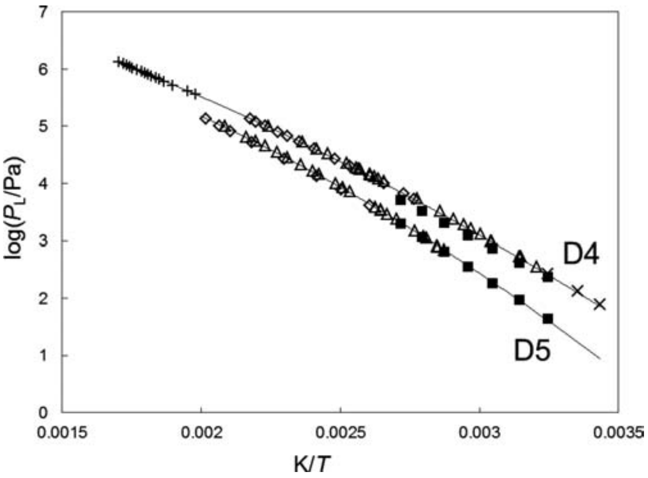

Figure 2. Relationship between the logarithm of the liquid state vapor pressure and reciprocal temperature of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) as reported here, ■, and by ◇, Flaningam;[13] ×, Marsh;[23] +, Young;[24] and △, Palczewska-Tulinska and Oracz.[25] The lines are fitted quadratic functions that serve to guide the eye.

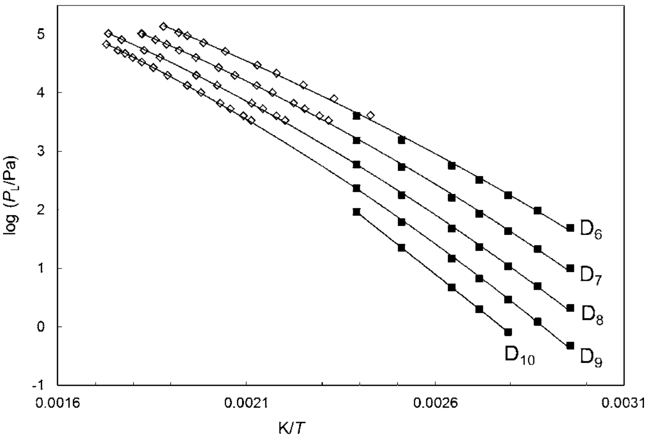

Figure 3. Relationship between the logarithm of the liquid state vapor pressure and the reciprocal temperature of cyclic dimethylsiloxane oligomers as reported here, ■, and by Flaningam,[13] ◇. The lines are fitted quadratic functions that serve to guide the eye.

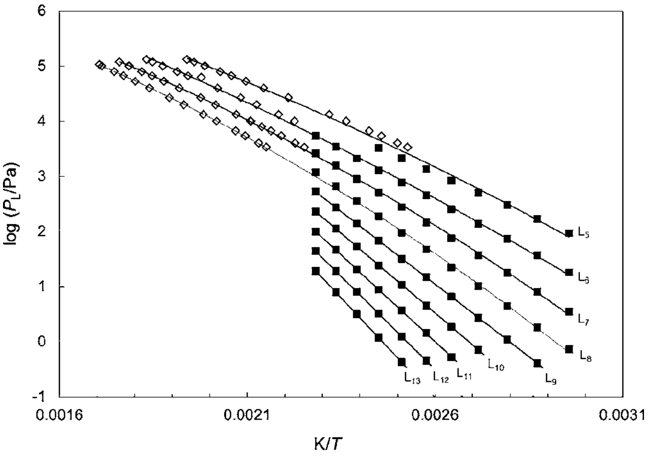

Figure 4. Relationship between the logarithm of the liquid state vapor pressure and reciprocal temperature of linear dimethylsiloxane oligomers as reported here, ■, and by Flaningam,[13] ◇. The lines are fitted quadratic functions that serve to guide the eye.

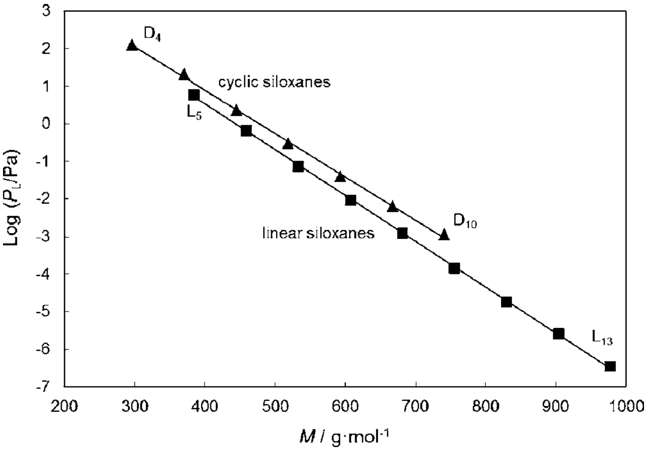

Figure 5. Relationship between the logarithm of the liquid state vapor pressure at 298.15 K and the molecular mass of cyclic, ▲, and linear, ■, dimethylsiloxane oligomers.

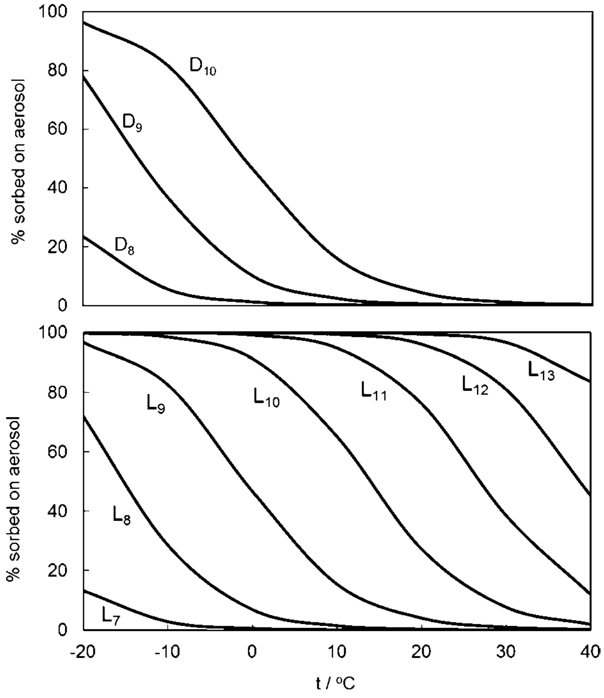

Figure 6. Fractions of different cyclic (top) and linear (bottom) dimethylsiloxane oligomers sorbed to aerosol as a function of temperature as estimated by the Junge−Pankow relationship.

Aerosol-Vapor Partitioning. The availability of vapor pressure data for the dimethylsiloxane oligomers allows us to estimate their tendency to sorb to aerosol as a function of temperature by using the Junge−Pankow relationship:[26]

$$\Phi = cS_T/(P_L + cS_T) \qquad (12)$$

where Φ is the fraction of the chemical sorbed to aerosols, c is a contaminant and aerosol-specific parameter, and S_T is the total surface area of the aerosol. In the calculation of Φ as displayed in Figure 6, we assumed that c is 0.172 Pa·m and S_T is $1.5 \cdot 10^{-4}$ m^{-1}, which is typical of the aerosol load in continental background air.[26] A higher particle load typically encountered indoors or in contaminated urban air would result in a shift of the curves to the right.

The results of these estimations suggest that only oligomers with more than eight dimethylsiloxane units are expected to sorb appreciably to aerosol at temperatures typically prevailing in the lower atmosphere. L_8 and D_9 only do so at freezing temperatures. The partitioning behavior of L_{10} and D_{10} is predicted to be highly dependent on ambient temperature. Oligomers smaller than L_7 and D_8 are not expected to sorb notably to aerosols. A recent study on dimethylsiloxanes in house dust noted a prevalence of the longer linear oligomers, whereas the smaller cyclic oligomers that are found in much higher levels in consumer products were less abundant.[2] This is consistent with our estimation of phase partitioning: small oligomers abundant in consumer products would be expected to be gas phase compounds in an indoor environment, whereas the longer linear oligomers would be expected to sorb to indoor dust at room temperatures.

Conclusions

New vapor pressure data for cyclic and linear dimethylsiloxane oligomers have been presented that are in excellent agreement with previously reported data but extend those to lower temperatures and larger oligomer sizes. For the estimation of the vapor pressure of dimethylsiloxane oligomers at environmentally relevant temperatures we recommend the use of eq 9 in combination with the m_L and b_L values reported in Table 1.

Acknowledgment

We thank Shihe Xu from Dow Corning for the donation of the dimethylsiloxane oligomer mixtures.

Supporting Information Available:

Triplicate retention times for the compounds for which tridecane, octadecane, and pentadecane serve as the standard reference compound (Tables S1, S2, and S3, respectively) and for linear alkanes that served as the standard reference and calibration compounds (Table S4) and vapor pressure data for the used calibration compounds (Table S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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