Silicate Esters and Related Compounds

Second in a series on silicate esters and related compounds. The first appeared in *J. Am. Chem. Soc.* **80**, 1737 (1958).

Method for Calculating the Boiling Points of Tetraalkoxysilanes and Hexaalkoxydisiloxanes

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THE INCREASING importance of silicates and disiloxanes as high temperature hydraulic fluids, heat transfer agents and lubricants makes it desirable to have a convenient empirical method for the calculation of the normal boiling point.

Such a method has been developed by a modification of the Kinney equation. The calculated values for a number of tetraalkoxysilanes and hexaalkoxydisiloxanes are closely correlated with the observed boiling points.

DISCUSSION

Several attempts have been made to find a method of correlating boiling points and molecular structure (3, 5, 7). The correlation of Kinney (6) is applicable to a wide variety of organic compounds. He developed the formula

$$\text{B.P. } (^\circ\text{ C.}) = 230.14\sqrt[3]{BPN} - 543$$

where *BPN* is the sum of the individual atomic and group boiling point numbers for the molecule. The equation was derived from the known boiling points of the normal paraffin hydrocarbons. The atomic boiling point numbers for carbon and hydrogen were chosen as 0.8 and 1.0, respectively.

Lewis and Newkirk (8) have applied the Kinney equation to many organosilicon compounds. Boiling point numbers were given for silicon and the following atoms and groups attached to silicon: H, Cl, Br, CH_3, C_2H_5, n-C_3H_7, and C_6H_5. They found it necessary to give hydrogen attached to silicon a value of 4.20. Furthermore, for a given group, the boiling point number varied with the degree of substitution on the central silicon atom. Thus, the value of CH_3— varied from 3.43 in CH_3SiH_3 to 2.74 in $(CH_3)_4Si$. Their method in its present form, however, is not applicable to silicon compounds containing oxygen or fluorine (8).

The Kinney equation can be extended to include the calculation of the normal boiling points of organic compounds containing both silicon and oxygen. This article describes its application to both straight- and branched-chain tetraalkoxysilanes and hexaalkoxydisoloxanes.

Straight-Chain Tetrallkoxysilanes. For the straight-chain tetraalkoxysilanes, the Lewis and Newkirk (8) atomic *BPN* values of 4.2 and 0.8 are used for silicon and carbon, respectively. For oxygen, Kinney's (6) value of 1.1, as assigned to ethers of the type $R_2CHOCHR_2$, is used. To provide good agreement with the experimental data, hydrogen is assigned the value of 0.7. Using tetraethoxysilane as an example, normal boiling point calculations by this method are made as follows: for $C_8H_{20}O_4Si$, $H = 20 \times 0.7 = 14$; $C = 8 \times 0.8 = 6.4$; $O = 4 \times 1.1 = 4.4$; and $Si = 1 \times 4.2 = 4.2$. The sum of these values gives a *BPN* value of 29.0. Using this value in the Kinney equation results in a calculated normal boiling point of 164.0°. The values reported in the literature are 165.3-5.8 (12) and 168.1 (2).

Similarly, boiling points are calculated for the homologous series of straight-chain tetraalkoxysilanes from the ethyl through the hexyl derivatives. The observed and calculated boiling points, with the individual atomic *BPN* calculations, are shown in Table I. Agreement between all observed and calculated boiling points is within 1.7% average deviation. A calculated normal boiling point is also given for $(C_6H_{13}O)_4Si$ even though this compound has not yet been reported in the literature nor prepared in this laboratory. The methyl derivative proved to be a special case. Therefore, a *BPN* value of 3.88 was assigned to each of the methyl groups in tetramethoxysilane.

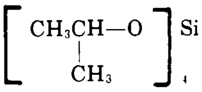
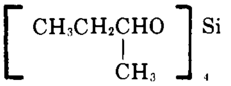
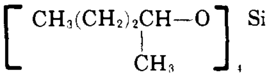
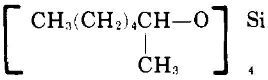
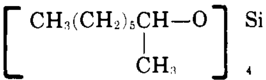
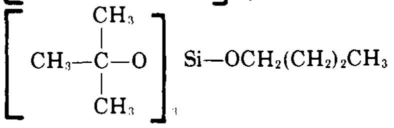
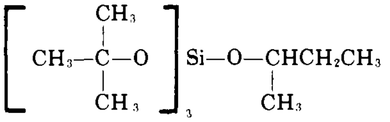
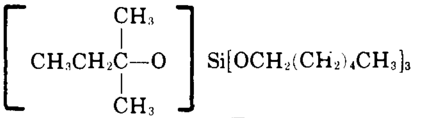
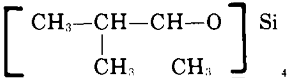
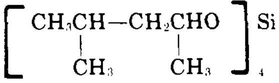
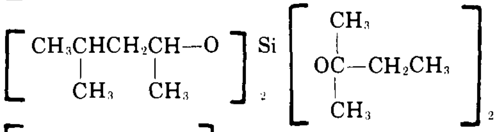
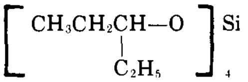
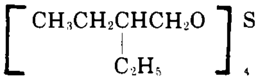
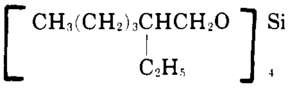
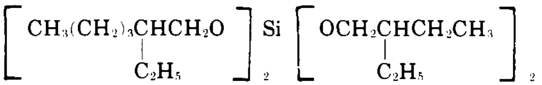
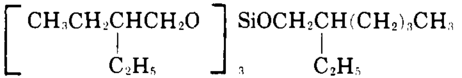
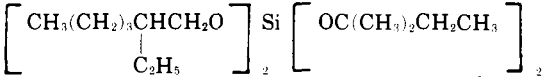
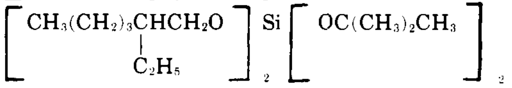
Branched-Chain Tetraalkoxysilanes. As is typical with organic compounds, the branched chain tetraalkoxysilanes have lower boiling points than the corresponding straight chain derivatives (in the present discussion all aliphatic radicals other than a straight chain primary group are considered as branched). Therefore, in applying the equation to branched chain derivatives, it is necessary to reduce the over-all contribution of the carbon and hydrogen atoms to the *BPN* for a given compound. In calculating the *BPN* for the tetraalkoxysilanes in this class, the longest straight chain in a branched alkyl group is assigned its normal value based upon carbon being 0.8 and hydrogen being 0.7. Thus, atoms or groups responsible for branching

Table I. Boiling Point Numbers for the Straight Chain Tetraalkoxysilanes

Compound	Boiling Point Numbers					B. P., ° C.		Deviation, ° C.
	H (0.7)	C (0.8)	Si (4.2)	O (1.1)	Total	Exptl.	Calcd.	
$(CH_3O)_4Si$	[a]	[a]	4.2	4.4	24.12	121.5[b]	121.5	0.0
$(CH_3CH_2O)_4Si$	14.0	6.4	4.2	4.4	29.0	165.5[c]	164.0	−1.5
$(CH_3CH_2CH_2O)_4Si$	19.6	9.6	4.2	4.4	37.8	226[d]	228.7	+ 2.7
$(CH_3CH_2CH_2CH_2O)_4Si$	25.2	12.8	4.2	4.4	46.6	275[e]	284.5	+ 9.5
$(CH_3CH_2CH_2CH_2CH_2O)_4Si$	30.8	16.0	4.2	4.4	55.4	340[f]	334.5	−5.5
$(CH_3CH_2CH_2CH_2CH_2CH_2O)_4Si$	36.4	19.2	4.2	4.4	64.2	[g]	378.5	...

[a] For methyl orthosilicate, CH_3— is 3.88. [b] (4). [c] (12). [d] (10). [e] (1).
[f] Converted from reduced pressure data as shown in Table IV. [g] Not reported in the literature.

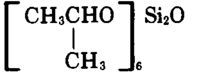
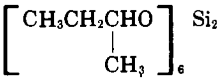
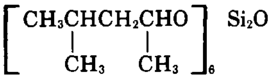
Table II. Boiling Point Numbers for Branched Chain Tetraalkoxysilanes

Compound	Boiling Point Number[a]					B. P., ° C.		Devi-ation, ° C.
	Straight Chain		Substituent					
	Name	Value	Name	Value	Total	Exptl.	Calcd.	
 $[\mathrm{CH_3CH(CH_3)-O}]_4\mathrm{Si}$	Ethyl	5.1	1-Methyl	1.00	33.0	190	194.3	+ 4.3
 $[\mathrm{CH_3CH_2CH(CH_3)O}]_4\mathrm{Si}$	Propyl	7.3	1-Methyl	0.90	41.4	251	252.6	+ 1.6
 $[\mathrm{CH_3(CH_2)_2CH(CH_3)-O}]_4\mathrm{Si}$	Butyl	9.5	1-Methyl	0.80	49.8	302	303.0	+ 1.0
 $[\mathrm{CH_3(CH_2)_4CH(CH_3)-O}]_4\mathrm{Si}$	Hexyl	13.9	1-Methyl	0.60	66.6	389	389.2	+ 0.2
 $[\mathrm{CH_3(CH_2)_5CH(CH_3)-O}]_4\mathrm{Si}$	Heptyl	16.1	1-Methyl	0.50	75.0	428	427.5	−0.5
 $[\mathrm{CH_3-C(CH_3)_2-O}]_3\mathrm{Si-OCH_2(CH_2)_2CH_3}$	Ethyl Butyl	5.1 9.5	1-Methyl	1.00	39.4	240	239.9	−0.1
 $[\mathrm{CH_3-C(CH_3)_2-O}]_3\mathrm{Si-O-CH(CH_3)CH_2CH_3}$	Ethyl Propyl	5.1 7.3	1-Methyl	1.00 0.90	38.1	230	230.0	±0.0
 $[\mathrm{CH_3CH_2C(CH_3)_2-O}]\mathrm{Si[OCH_2(CH_2)_4CH_3]_3}$	Propyl Hexyl	7.3 13.9	1-Methyl	0.90	59.4	362	355.0	−7.0
 $[\mathrm{CH_3-CH(CH_3)-CH(CH_3)-O}]_4\mathrm{Si}$	Propyl	7.3	1-Methyl 2-Methyl	0.90 1.20	46.4	286	282.7	−3.3
 $[\mathrm{CH_3CH(CH_3)-CH_2CH(CH_3)O}]_4\mathrm{Si}$	Butyl	9.5	1-Methyl 3-Methyl	0.80 1.08	54.12	332	327.6	−4.4
 $[\mathrm{CH_3CH(CH_3)CH_2CH(CH_3)-O}]_2\mathrm{Si}[\mathrm{OC(CH_3)_2-CH_2CH_3}]_2$	Propyl Butyl	7.3 9.5	1-Methyl (*tert*-Alkyl) 1-Methyl 3-Methyl	0.90 0.80 1.08	49.56	304	302.3	−1.7
 $[\mathrm{CH_3CH_2CH(C_2H_5)-O}]_4\mathrm{Si}$	Propyl	7.3	1-Ethyl	3.20	50.6	311	308.3	−2.7
 $[\mathrm{CH_3CH_2CH(C_2H_5)CH_2O}]_4\mathrm{Si}$	Butyl	9.5	2-Ethyl	3.40	60.2	358	358.9	+ 0.9
 $[\mathrm{CH_3(CH_2)_3CH(C_2H_5)CH_2O}]_4\mathrm{Si}$	Hexyl	13.9	2-Ethyl	2.72	75.08	419	430.2	+ 11.2
 $[\mathrm{CH_3(CH_2)_3CH(C_2H_5)CH_2O}]_2\mathrm{Si}[\mathrm{OCH_2CH(C_2H_5)CH_2CH_3}]_2$	Hexyl Butyl	13.9 9.5	2-Ethyl 2-Ethyl	2.72 3.40	67.64	390	394.0	+ 4.0
 $[\mathrm{CH_3CH_2CH(C_2H_5)CH_2O}]_3\mathrm{SiOCH_2CH(C_2H_5)(CH_2)_3CH_3}$	Butyl Hexyl	9.5 13.9	2-Ethyl 2-Ethyl	3.40 2.72	63.00	380	372.7	−7.3
 $[\mathrm{CH_3(CH_2)_3CH(C_2H_5)CH_2O}]_2\mathrm{Si}[\mathrm{OC(CH_3)_2CH_2CH_3}]_2$	Hexyl Propyl	13.9 7.3	2-Ethyl 1-Methyl	2.72 0.90	60.04	358	357.6	−0.4
 $[\mathrm{CH_3(CH_2)_3CH(C_2H_5)CH_2O}]_2\mathrm{Si}[\mathrm{OC(CH_3)_2CH_3}]_2$	Hexyl Ethyl	13.9 5.1	2-Ethyl 1-Methyl	2.72 1.00	56.04	337	337.0	±0.0

[a] For all calculations, Si = 4.2 and O = 1.1.

[b] Converted from reduced pressure data as shown in Table IV.

Table III. Boiling Point Numbers for Hexaalkoxydisiloxanes

	Boiling Point Number[a]										
	Straight Chain		Substituent		Sum of C, H, O			B. P., ° C.		
Compound	Name	Value	Name	Value	Original	Less 10%	Total	Exptl.	Calcd.	Dev., ° C.
$(CH_3CH_2O)_6Si_2O$	Ethyl	5.1	...	...	38.30	34.47	39.47	236[b]	240.0	+ 4.0
$(CH_3CH_2CH_2O)_6Si_2O$	Propyl	7.3	...	...	51.50	46.35	51.35	324[b]	312.4	−11.6
$[CH_3(CH_2)_2CH_2O]_6Si_2O$	Butyl	9.5	...	...	64.70	58.23	63.23	382[b]	373.9	−8.1
 $\left[CH_3\underset{\substack{\vert \\ CH_3}}{C}HO\right]_6 Si_2O$	Ethyl	5.1	1-Methyl	1.0	44.30	39.87	44.87	275[c]	274.9	−0.1
 $\left[CH_3CH_2\underset{\substack{\vert \\ CH_3}}{C}HO\right]_6 Si_2O$	Propyl	7.3	1-Methyl	0.90	56.90	51.21	56.21	339[c]	338.0	−1.0
 $\left[CH_3\underset{\substack{\vert \\ CH_3}}{C}HCH_2\underset{\substack{\vert \\ CH_3}}{C}HO\right]_6 Si_2O$	Butyl	9.5	1-Methyl 3-Methyl	0.80 1.08	75.98	68.38	73.38	418[c]	420.0	+ 2.0

[a] Value of Si = 2.5; values for C, H, O, same as in alkyl orthosilicates.
[b] (*1*).
[c] Converted from reduced pressure data as shown in Table IV.

Table IV. Analytical and Physical Data on Tetraalkoxysilanes and Hexaalkoxydisiloxanes[a]

Compound	Refractive Index N_D^{20}	$d\frac{20}{4}$	Molar Refraction Calcd.[b]	Molar Refraction Found	Boiling Point ° C.	Boiling Point Mm. Hg.
Tetra(2-propoxy)silane	1.3852	0.8746	70.37	70.89	70.5	10
Tetra(2-butoxy)silane	1.4075	0.8871	88.81	89.04	105	5
Tri(1,1-dimethylethoxy)(2-butoxy)silane	1.4024	0.8806	88.81	88.73	89	5
Tri(1,1-dimethylethoxy)(1-butoxy)silane	1.4012	0.8718	88.81	89.37	97.5	5
Tetra(1-pentoxy)silane	...	...	...	...	144	1[c]
Tetra(2-pentoxy)silane	1.4170	0.8799	107.28	107.65	114	1
Tetra(3-pentoxy)silane	...	...	...	...	121	1[d]
Tetra(3-methyl-2-butoxy)silane	1.4182	0.8880	107.28	106.94	132-135	5
Di(4-methyl-2-pentoxy)di(1,1-dimethylopropoxy)silane	1.4207	...	...	...	146	5[e]
Di(2-ethylhexoxy)di(1,1-dimethylpropoxy)silane	1.4312	0.8842	134.99	134.95	153	1[f]
Tri(1-hexoxy)(1,1-dimethylpropoxy)silane	1.4261	...	...	...	160	1[g]
Tri(2-ethylbutoxy)(2-ethylhexoxy)silane	1.4328	0.8885	134.99	134.74	176	1.1
Tetra(2-ethyl-1-butoxy)silane	1.4307	0.8920	125.75	125.48	166-171	2
Di(2-ethylbutoxy)di(2-ethylhexoxy)silane	1.4348	0.8859	144.22	143.94	175-177	1
Tetra(4-methyl-2-pentoxy)silane	1.4205	0.8669	125.75	126.45	136	1
Di(2-ethylhexoxy)di(1,1-dimethylethoxy)silane	1.4239	0.8789	125.75	125.62	139	1[h]
Tetra(2-heptoxy)silane	1.4296	0.8715	144.22	144.79	176	1
Tetra(2-octoxy)silane	1.4340	0.8692	162.70	163.28	204	1
Tetra(2-ethyl-1-hexoxy)silane	1.4388	0.8803	162.70	162.77	194	1
Hexa(2-propoxy)disiloxane	1.3930	0.9281	109.15	109.72	96	1
Hexa(2-butoxy)disiloxane	1.4133	0.9285	136.86	137.26	146	1.5[i]
Hexa(4-methyl-2-pentoxy)disiloxane	1.4252	0.9048	192.27	192.02	194	1

[a] For methods of synthesis refer to Wright and others (*14*).
[b] Calculations based on values of Sauer (*1*) and Warrick (*13*).
[c] Synthesis reaction, $4\ CH_3(CH_2)_3CH_2OH + SiCl_4 \rightarrow 4HCL + [CH_3(CH_2)_3CH_2O]_4Si$; qualitative test showed no Cl present in distilled reaction product.
[d] Synthesis reaction, $4\ (CH_3CH_2)_2CHOH + SiCl_4 \rightarrow 4HCL + [(CH_3CH_2)_2CHO]_4\ Si$; qualitative test showed no Cl present in distilled reaction product.
[e] % Si calcd. 6.94, found 6.75.
[f] % Si calcd. 6.10, found 6.11.
[g] % Si calcd. 6.71, found 6.61.
[h] % Si calcd. 6.49, found 6.55.
[i] % Si calcd. 11.00, found 10.52.

are then treated as substituents. The contribution that a given substituent makes to the *BPN* is dependent upon the position of the substituent on the straight chain—that is, No. 1 or some position other than 1—and the length of the straight chain to which the substituent is attached. Basic values for the simplest substituent, the methyl radical, are assigned as 1.0 for the 1-position and 1.2 for any position other than the 1-position. For larger substituents, the normal C—H values for the additional atoms are added to the appropriate methyl value. Thus, a 1-ethyl group would have a value of $CH_3 = 1.0$; $C = 0.8$; $2H = 1.4$; or a total value of 3.2.

The effect of a given radical on the boiling point of tetraalkoxysilanes decreases as the molecular weight of the parent molecule increases. Thus, for branched chain alkyl groups, the contribution of a given substituent to the *BPN* of the compound is reduced as the straight chain portion increases in length. For the shortest possible straight chain, the substituent is given the full value. For each additional carbon atom in the chain, the contribution of a given substituent is reduced by 10% but in no case by more than 50% of its highest possible value. The following examples demonstrate the method of calculating the contribution of various branched chain alkyl groups.

	Straight Chain		Substituent	
Alkyl Group	Name	Value	Name	Value
$CH_3CH(CH_3)$—	Ethyl	5.1	1-Methyl	1.0
$CH_3CH_2CH(CH_3)$—	Propyl	7.3	1-Methyl	0.9
$CH_3CH_2CH(C_2H_5)$—	Propyl	7.3	1-Ethyl	3.2
$CH_3CH(CH_3)CH_2$—	Propyl	7.3	2-Methyl	1.2
$CH_3CH_2CH(C_2H_5)CH_2$—	Butyl	9.5	2-Ethyl	3.4

The boiling point numbers of 18 branched chain tetraalkoxysilanes were calculated by this method. The normal boiling points were then calculated from the equation and compared to the observed values, and average deviations between calculated and observed values were within 1.0% (TableII).

Hexaalkoxydisiloxanes. As molecular complexity increases, the contribution of a given atom or group to the *BPN* of the molecule can be expected to decrease. Fixed values for carbon, hydrogen, oxygen, and silicon apply to the straight chain tetraalkoxysilanes. With the branched-chain derivatives, it is necessary to introduce a system for reducing the carbon and hydrogen values based on molecular complexity, but fixed values of silicon and oxygen are permissible. However, with the more complex hexaalkoxydisiloxane structures, all atomic and group *BPN* values must be reduced. For this class, silicon is assigned a value of 2.5 instead of 4.2. All other atomic (C,H,O) and group values are reduced by 10% from the value calculated by the methods applicable to straight and branched chain tetraalkoxysilanes. The application of the method to six straight and branched-chain hexaalkoxydisiloxanes is shown in Table III. Values are presented for the straight chains, the substituents, and the total *BPN*. In addition, observed and calculated boiling points are given, as well as the deviation. All observed and calculated boiling points are within 1.4% average deviation.

With the exception of the first four compounds in Table I, all normal boiling point data were converted from reduced pressure distillations by using the vapor pressure-temperature nomographs of Lippincott and Lyman (*9*). The most consistent results were obtained by converting with the Group III classification. No attempts were made to convert boiling points from distillations at less than 1 mm. pressure. Wherever possible, higher pressures were used. Boiling point data, as well as analytical data for compounds prepared in this laboratory and not previously reported in the literature, are shown in Table IV.

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