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Vapor−Liquid Critical Properties of Some Tetraalkoxysilanes

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The critical pressures and the critical temperatures of ten tetraalkoxysilanes (tetraalkyl esters of silicic acid) $Si[O(CH_2)_nH]_4$ with $n = 1$ to 10 have been measured. All the substances studied begin to decompose at temperatures below their critical points. The method of pulse-heating applicable to thermally unstable compounds has been used. Residence times were from (0.03 to 1) ms, which resulted in little decomposition of the substances during measuring. The experimental critical properties of tetraalkoxysilanes have been compared with the values estimated by the group-contribution methods of Lydersen and Nannoolal et al.

Introduction

Tetraalkoxysilanes (tetraalkyl esters of silicic acid) $Si[O(CH_2)_nH]_4$ are widely used in many applications as liquid polymers, as glues, as lacquers, as start materials for forming mesaporous silica oxide structures, for stabilizing thermoplastic polycarbonates, etc. This paper presents the critical temperatures and pressures of tetraalkoxysilanes with straight alkyl chains from tetramethoxy- ($n = 1$) to tetradecoxysilane ($n = 10$). Previously, the critical constants were measured only for tetramethoxy-, tetraethoxy-, and tetrapropoxysilanes.[1] Alkoxysilanes that contain $SiOCH_3$ or $SiOC_2H_5$ groups are known to decompose at temperatures higher than 475 K, and the thermal stability of alkoxysilanes decreases with increasing length of the alkyl chain.[2] The critical temperatures of tetraalkoxysilanes measured are from (558 to 849) K. Therefore, it is reasonable to assume that all the tetraalkoxysilanes studied are thermally unstable at their critical points. The pulse-heating method with ultralow residence times applicable to unstable compounds was used for the measurements.

Experimental Section

Materials. Samples of tetraalkoxysilanes were synthesized, purified, and analyzed at the Institute of Organic Synthesis of RAS (Ekaterinburg) under the leadership of Dr. Yuri Yatluk. The alkoxysilanes were prepared by transesterification of tetramethoxysilane or tetraethoxysilane with 1-alkanols. For example, $Si[OCH_3]_4$ (1 mol) was transesterified with 1-decanol containing sodium decylate (0.017 mol) as a catalyst. The mixture was refluxed for 2 h. The methanol was distillated, and the residue was fractioned at vacuum. The yield was from (60 to 70) %. Before and after the critical properties measurements, the purities of the samples were determined by proton magnetic spectroscopy (Bruker DRX 400). Table 1 gives the Chemical Abstract Service Registry Numbers (CASRN) of the tetraalkoxysilanes studied and the purities of the samples. The purity of the samples is not significantly changed in the course of measuring the critical properties.

Table 1. Purities of Compounds Used in Critical Point Measurement

compound	CASRN[a]	purity/% before measuring critical constants	purity/% after measuring critical constants
tetramethoxysilane	681-84-5	99.9	99.9
tetraethoxysilane	78-10-4	99.9	99.9
tetrapropoxysilane	682-01-9	99.9	99.8
tetrabutoxysilane	4766-57-8	99.9	99.9
tetrapentoxysilane	6382-12-3	99.9	99.9
tetrahexoxysilane	7425-86-7	99.8	99.7
tetraheptoxysilane	18759-42-7	99.9	99.9
tetraoctoxysilane	78-14-8	99.9	99.9
tetranonoxysilane	18817-76-0	99.9	99.8
tetradecoxysilane	18845-54-0	99.9	99.9

[a] Chemical Abstracts Service Registry Number.

Method. The technique used here for measuring the critical constants has previously been extensively used by our group. It has proven to be reliable and useful for compounds that decompose significantly near their critical temperatures. The pulse-heating apparatus and procedure have been described in detail in previous publications.[3–5] A liquid under study filled a thin-walled Teflon cup, and the pressure outside the cup was created by a press and measured by a dial gauge. A platinum wire probe, $2 \cdot 10^{-3}$ cm in diameter and (1 to 3) cm in length, was placed in the liquid. The probe was heated by pulses of electric current in such a way that by the end of a pulse the probe and the thin liquid layer near it were heated to the temperature of spontaneous boil-up (attainable superheat). The time from the start of a pulse to the moment of boil-up was from (0.03 to 1.0) ms. At the moment of boil-up, a probe temperature perturbation arises from an abrupt change of the conditions of heat transfer from the probe to the liquid. The probe temperature was determined from its resistance at that moment. The probe temperature perturbation may be both positive and negative. The pressure in the liquid increased until the negative temperature perturbation

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dropped to the level of the apparatus sensitivity ($1 \cdot 10^{-3}$ K). This pressure was taken to be equal to the measured value of the critical pressure p_c^m, and the temperature of the attainable superheat at this pressure was taken to be equal to the measured value of the critical temperature T_c^m. The values of p_c^m and T_c^m are always lesser than the true critical properties and require correction. It is an inherent feature of the pulse-heating method that cannot be removed by modification of the apparatus. The true critical constants of a stable compound were calculated from the following equations

$$p_c = p_c^m/\pi_o, T_c = T_c^m/\tau_0 \qquad (1)$$

where $1/\pi_0$ and $1/\tau_0$ are correction factors.[3] To calculate the correction factors, the thermophysical properties of the liquid and the vapor phase near the critical point are required. These properties are calculated by the principle of corresponding states using the formulas given in a previous paper.[6] The formulas contain a similarity parameter of the compound under study: the acentric factor or the analogous parameter suggested by Filippov[7]

$$A = 100\frac{p_{vp}(T/T_c = 0.625)}{p_c}$$

where p_{vp} is the vapor pressure at a reduced temperature equal to 0.625.

The Filippov parameters and the critical properties of alkoxysilanes were calculated by an iteration method. For the first iteration, p_c^m and T_c^m were used as the critical constants. The vapor pressure of the tetraalkoxysilanes with $n = 1$ to 4 was estimated by the following equation

$$\ln p_{vp} = B - \frac{C}{T}$$

The parameters B and C were calculated from the values of p_c^m and T_c^m and the normal boiling points. The normal boiling temperatures were taken for tetramethoxy- and tetraethoxysilanes from the NIST Chemistry WebBook,[8] for tetrapropoxysilane from the paper by Myers and Danner,[9] and for tetrabutoxysilane according to the Sigma-Aldrich recommendations.[10] We failed to find any information about the vapor pressure of heavier tetraalkoxysilanes. The Filippov parameters of tetraalkoxysilanes with $n = 5$ to 10 were estimated using the equation suggested in our previous paper[11]

$$\ln A = a + bn^{2/3}$$

Then, from the values of π_0 and τ_0 and using eq 1, p_c and T_c were calculated. For the second iteration, the Filippov parameter and the critical temperature and pressure were calculated using the values obtained after the first iteration. Two iterations were enough because the values of π_0 and τ_0 are little affected by the variations of Filippov's parameter.

For calculating the correction factors, two additional quantities are needed: the factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation in a superheated liquid, and the ideal gas heat capacity of a compound under investigation. The factor G_T was measured in one experiment with the critical constants as described previously[3] and estimated at 1.5 K^{-1}. The ideal gas heat capacity was estimated using the atomic contribution method by Harrison and Seaton[12] with the contribution for silicon recommended by Myers and Danner.[9]

The apparent critical temperature and pressure of a thermally unstable compound determined as described above may depend on the time from the beginning of a heating pulse to the moment of boiling-up, t^*, due to the decomposition of a compound under study in the course of heating. The critical properties of tetraalkoxysilanes were measured with the help of probes (1, 2, and 3) cm in length at heating times t^* = (0.03, 0.06, 0.11, 0.22, 0.45, and 1.00) ms. Two to four samples of each compound were used in the experiments. The tetraalkoxysilanes studied are unstable at their critical points. However, in our experiments, the tetraalkoxysilanes showed no evidence of decomposition, and no dependence of the apparent critical properties on the heating time t^* was found; therefore, the experimental data were averaged over all the probe lengths, heating times, and samples.

Table 2. Normal Boiling Points and Critical Temperatures of Tetraalkoxysilanes: Experimental Values and Comparison with Predictive Methods

	T_b/K		T_c/K		
compound	exptl	calcd, ref 17	exptl	ref 9	ref 16
tetramethoxysilane	394.5[a]	394.3	558 ± 6[d] 562.8 ± 0.2[e]	547.2	580.0
tetraethoxysilane	442[a]	450.0	587 ± 6[d] 592.2 ± 0.2[e]	578.5	600.0
tetrapropoxysilane	502[b]	519.7	649 ± 6[d] 647.7 ± 0.4[e]	631.8	653.7
tetrabutoxysilane	548[c]	578.2	682 ± 7[d]	674.8	688.1
tetrapentoxysilane		628.9	714 ± 7[d]		765.0
tetrahexoxysilane		673.9	757 ± 8[d]		797.0
tetraheptoxysilane		714.5	778 ± 8[d]		824.1
tetraoctoxysilane		751.6	812 ± 8[d]		847.8
tetranonoxysilane		785.9	830 ± 8[d]		868.7
tetradecoxysilane		817.8	849 ± 8[d]		887.6
AAPE/%[f]				1.8	4.0
MAPE/%[g]				2.7	7.1

[a] Ref 8. [b] Ref 9. [c] Ref 10. [d] This work. [e] Ref 1. [f] AAPE = $(1/N)(\Sigma|Y_c^{exptl} - Y_c^{calcd}|/Y_c^{exptl})$, where N is the number of experimental data points, Y_c^{exptl} is the experimental value of the critical property, and Y_c^{calcd} is the calculated value of the critical property. [g] MAPE = $(|Y_c^{exptl} - Y_c^{calcd}|_{max}/Y_c^{exptl})$.

Table 3. Critical Pressures p_c/MPa of Tetraalkoxysilanes: Experimental Values and Comparison with Predictive Methods

compound	exptl	ref 9	ref 16
tetramethoxysilane	2.89 ± 0.09[a] 2.873 ± 0.007[b]	2.779	2.975
tetraethoxysilane	2.04 ± 0.06[a] 2.045 ± 0.007[b]	1.981	2.017
tetrapropoxysilane	1.37 ± 0.04[a] 1.696 ± 0.007[b]	1.539	1.508
tetrabutoxysilane	1.10 ± 0.03[a]	1.259	1.168
tetrapentoxysilane	0.89 ± 0.03[a]	1.064	0.930
tetrahexoxysilane	0.79 ± 0.02[a]	0.922	0.758
tetraheptoxysilane	0.74 ± 0.02[a]	0.813	0.628
tetraoctoxysilane	0.66 ± 0.02[a]	0.728	0.529
tetranonoxysilane	0.61 ± 0.02[a]	0.658	0.451
tetradecoxysilane	0.60 ± 0.02[a]	0.601	0.389
AAPE		8.7	12.6
MAPE		16.5	35.2

[a] This work. [b] Ref 1.

Uncertainties. The uncertainties of the critical constants measured by the pulse-heating method were discussed in detail in our previous papers.[13,14] We estimate the uncertainties for tetraalkoxysilanes investigated at $0.03p_c$ and $0.01T_c$, where T_c is the absolute temperature. It corresponds to an uncertainty from (± 0.09 to ± 0.02) MPa for the critical pressure and from (± 6 to ± 8) K for the critical temperature.

Results and Discussion

The critical temperatures and pressures of tetraalkoxysilanes included in this study are given in Tables 2 and 3 and Figure 1. These tables and the figure also contain the critical constants of tetramethoxy-, tetraethoxy-, and tetrapropoxysilanes measured

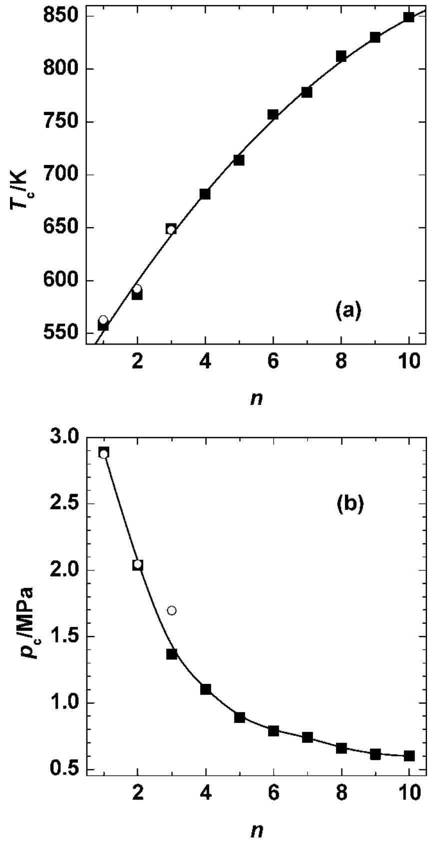

Figure 1. Critical temperatures (a) and pressures (b) of tetraalkoxysilanes $Si[O(CH_2)_nH]_4$ vs the number of CH_2 groups *n* in the alkyl radical. ■, this work; ○, ref 1.

by Waterson and Young.[1] In Tables 2 and 3, the experimental values of the critical properties are shown together with their uncertainties. The difference between our values of the critical temperatures and those by Waterson and Young does not exceed the combined uncertainties. The situation with the critical pressure is more complex. The critical pressures of tetramethoxy- and tetraethoxysilanes obtained by us and Waterson and Young are very close to each other, but the critical pressure of tetrapropoxysilane determined by Waterson and Young is considerably higher than ours. A possible reason for this may be greater thermal decomposition of tetrapropoxysilane in the experiments of Waterson and Young. They write nothing about decomposition of tetraalkoxysilanes in the course of their experiments. However, against this explanation is the fact that the critical temperatures of this compound obtained by us and Waterson and Young practically coincide.

According to the well-known correlation by Lydersen,[15] the quantity $(M/p_c)^{1/2}$ should be a linear function of the number of CH_2 groups in a molecule for a given homologous series. Here *M* is the molar mass. However, for tetraalkoxysilanes, a quadratic equation works better

$$\{[M/(\mathrm{kg \cdot mol^{-1}})]/[p_c/\mathrm{MPa}]\}^{1/2} = 0.0998 + 0.1217n - 0.0026n^2 \quad (2)$$

The solid line in Figure 2 corresponds to eq 2.

Most of the well-known group-contribution methods do not apply to tetraalkoxysilanes because they do not have contributions for silicon atoms and groups containing silicon. In fact, we found in the literature only two methods: the method by Lydersen[15] with group and atomic contributions determined by Myers and Danner[9] and that by Nannoolal et al.[16] Both of the methods require the normal boiling points to calculate the critical temperatures. We know experimental normal boiling temperatures only for four tetraalkoxysilanes from tetramethoxy- to tetrabutoxysilane. For these alkoxysilanes, the critical temperatures were calculated using experimental normal boiling points. For the rest of the alkoxysilanes the normal boiling temperatures were estimated by the method suggested by Nannoolal et al.[17] Table 2 shows that the discrepancy between experimental and calculated values of the normal boiling temperature increases progressively with increasing number of CH_2 groups in a molecule of tetraalkoxysilane and achieves about 30 K for tetrabutoxysilane. One may suggest that this discrepancy will hardly be lesser for heavier tetraalkoxysilanes. For the reason of unsatisfactory estimates of the normal boiling points, we calculated the critical temperatures of tetrapentoxy- to tetradecoxysilane using only the method by Nannoolal et al.[16] The idea was as follows. The methods of the estimation of the normal boiling temperature and the critical temperature suggested by Nannoolal et al. are the two parts of one approach and use the same set of structural groups, whereas in the Lydersen method, another set of groups is used.

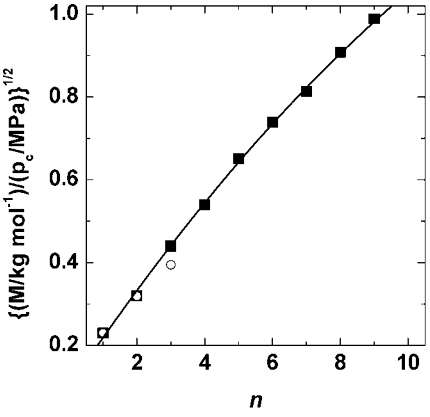

Figure 2. Correlation of the critical pressure of tetraalkoxysilanes $Si[O(CH_2)_nH]_4$ as a function of the number of CH_2 groups *n* in the alkyl radical and molar mass *M*. ■, this work; ○, ref 1. The solid line corresponds to eq 2.

The critical properties of tetraalkoxysilanes calculated in such a way are given in Tables 2 and 3. Percent deviations of the calculated values from the experimental critical constants are shown in Figure 3. If the experimental normal boiling temperatures are used, both estimation methods give reasonable critical temperature estimates that compare favorably with experimental critical temperature data. The average absolute percent deviation (AAPE) is equal to 1.8 % and 1.9 % for the estimation methods by Lydersen and Nannoolal et al., respectively. For tetraalkoxysilanes from tetrapentoxy- to tetradecoxysilane when the estimated normal boiling points are used, AAPE is considerably greater and exceeds 5.3 %. The critical pressure is predicted by the Lydersen method to be better than the method of Nannoolal et al. AAPE is equal to 8.7 % for the method by Lydersen against 12.6 % for that by Nannoolal et al.

Conclusion

The critical temperatures and pressures of tetraalkoxysilanes $Si[O(CH_2)_nH]_4$ with $n = 1$ to 10 have been measured. Previously, the experimental critical constants were available only for tetramethoxy-, tetraethoxy-, and tetrabutoxysilanes. The critical properties of tetraalkoxysilanes have also been estimated by the group-contribution methods of Lydersen and Nannoolal et al. For tetraalkoxysilanes from tetramethoxy- to tetra-

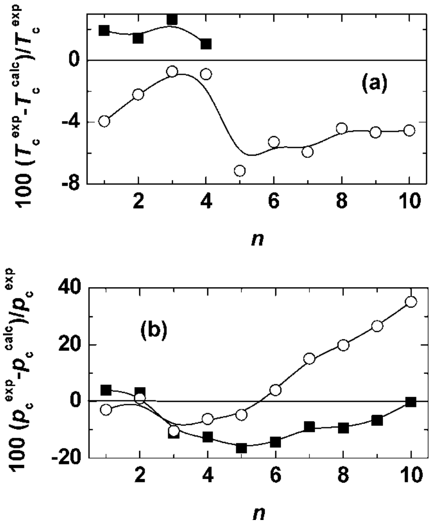

Figure 3. Percent deviations of the experimental critical temperatures (a) and pressures (b) of tetraalkoxysilanes Si[O$(CH_2)_n$H]$_4$ from the values calculated by group contribution methods as a function of the number of CH_2 groups in the alkyl radical n. GC methods: ■, ref 9; ○, ref 16.

propoxysilane, when the experimental normal boiling temperatures are used, both estimation methods give reasonable critical temperature estimates. For tetraalkoxysilanes from tetrapentoxy- to tetradecoxysilane, the normal boiling points and then the critical temperatures have been estimated using the method of Nannoolal et al. In this case, the calculated critical temperatures are considerably higher than the experimental ones. The critical pressure is predicted by the Lydersen method to be better than the method of Nannoolal et al.

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