

Critical Temperatures and Pressures of Some Tetraalkoxytitaniums

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The critical pressures and the critical temperatures of nine tetraalkoxytitaniums, $\text{Ti}[\text{O}(\text{CH}_2)_n\text{H}]_4$ with $n = 2$ to 10, have been measured. All of 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 0.46) ms, which resulted in little decomposition of the substances during measuring. The contributions of the titanium(IV) atom in the group contribution methods of Constantinou and Gani and Marrero and Gani have been calculated from the experimental data. The critical pressures and temperatures of tetraalkoxytitaniums have been estimated by these methods.

Introduction

This paper is a part of our investigation of the critical properties of compounds with symmetric star-like molecules. It may appear strange, but for hydrocarbons with such a structure of molecules, the experimental critical constants are known only for methane¹ and 2,2-dimethylpropane.² The main reason of this is the difficulties of obtaining pure samples of such hydrocarbons. It is much easier to synthesize and purify compounds with the general formula $\text{M}[\text{O}(\text{CH}_2)_n\text{H}]_4$, where for M may stand for Si, Ti, Zr, and so forth. The critical temperatures and pressures of tetraalkoxysilanes $\text{Si}[\text{O}(\text{CH}_2)_n\text{H}]_4$ from tetramethoxy- ($n = 1$) to tetradecoxysilane ($n = 10$) were measured by us previously.³ Tetraalkoxytitaniums themselves are an interesting object for measurements of the critical properties because they are widely used as reagents and catalysts in organic synthesis, as the source for forming nanoparticles and mesoporous structures of titanium dioxide, and so forth.⁴ To our knowledge, the critical properties of tetraalkoxytitaniums have never been measured before. The paper gives the critical temperatures and pressures of nine tetraalkoxytitaniums, $\text{Ti}[\text{O}(\text{CH}_2)_n\text{H}]_4$, from tetraethoxy- ($n = 2$) to tetradecoxytitanium ($n = 10$).

The thermal stability of alkoxytitaniums depends on the size and the structure of the alkyl radical. In general, alkoxytitaniums that are derivatives of branched alcohols begin to decompose at lower temperatures than the appropriate derivatives of normal alcohols.⁵ The lowest alkoxytitaniums $\text{Ti}[\text{OR}]_4$ (as R is C_5H_{11} or lower) were considered stable enough to be distilled at atmospheric pressure. However, later it was shown that, for instance, the decomposition of tetrabutoxytitanium went already at temperatures of (523⁶ and 553) K.⁷ Thus, distillation at atmospheric pressure is always accompanied by some decomposition.⁶

The critical temperatures of tetraalkoxytitaniums measured by us are from (647 to 882) K. Therefore, it is reasonable to assume that all of the tetraalkoxytitaniums studied are thermally

Table 1. Purities of Compounds Used in Critical Point Measurement

compound	purity/%	
	before measuring critical constants	after measuring critical constants
tetraethoxytitanium	99.9	99.9
tetrapropoxytitanium	99.9	99.8
tetrabutoxytitanium	99.9	99.9
tetrapentoxytitanium	99.9	99.9
tetrahexoxytitanium	99.8	99.8
tetraheptoxytitanium	99.9	99.7
tetraoctoxytitanium	99.9	99.9
tetranonoxytitanium	99.9	99.9
tetradecoxytitanium	99.9	99.9

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 tetraalkoxytitaniums were synthesized, purified, and analyzed at the Institute of Organic Synthesis of the Russian Academy of Sciences (Ekaterinburg). The tetraalkoxytitaniums were prepared by transesterification of tetraethoxytitanium with 1-alkanols. For example, $\text{Ti}[\text{OC}_2\text{H}_5]_4$ (1 mol) was transesterified with 1-octanol (4.5 mol). The mixture was refluxed for 3 h. The ethanol was distilled, and the residue was fractionated at vacuum. The yield was from (55 to 90) %. Before and after the measurements of the critical properties, the purities of the samples were determined by proton magnetic spectroscopy (Bruker DRX 400). Table 1 gives the purities of the samples. The purity of the samples is not significantly changed in the course of measuring the critical properties. It is not surprising because in our experiments only a thin liquid layer adjoining the wire probe is heated during a pulse of electric current. The thickness of this layer is (10^{-6} to 10^{-5}) m, and its volume V_1 is approximately 10^{-11} m³; the volume V_2 of the whole sample is

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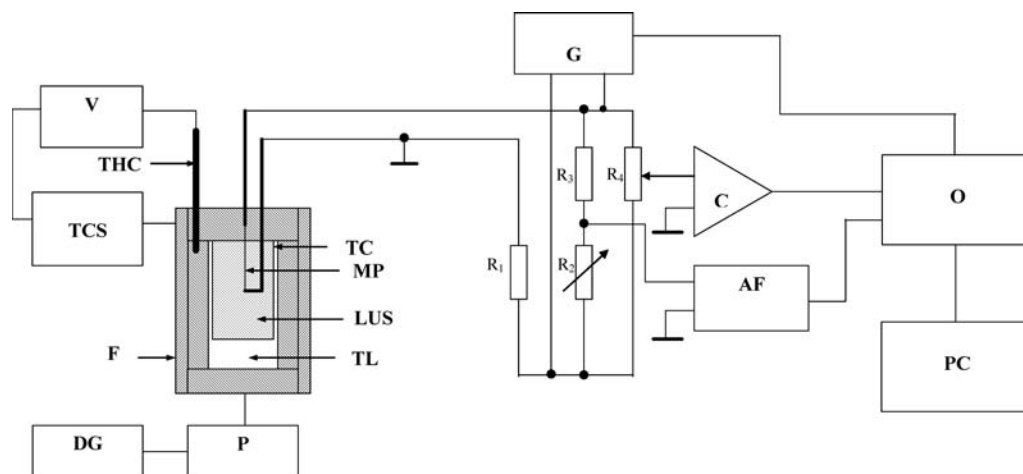


Figure 1. Block diagram of the apparatus for the measurement of the critical temperature and pressure by the pulse-heating method. AF, amplifying filter; C, comparator; DG, dial gauge; F, furnace; G, generator; LUS, liquid under study; MP, measuring probe; O, digital oscilloscope; P, press; PC, personal computer; TC, Teflon cup; TCS, temperature control system; THC, thermocouple; TL, liquid, transmitting pressure; V, digital voltmeter.

about 10^{-6} m³. Since $V_1 \ll V_2$, the mole fraction of decomposition products in the volume of the whole sample is very small. A decrease in the purity of tetrapropoxy-, tetrahexoxy-, and tetraheptoxytitaniums is probably connected with accidental causes and is close to the uncertainty of the PMS (proton magnetic spectroscopy) method, which is about 0.1 %.

Method. The technique employed in this study to measure the critical temperatures and pressures of tetraalkoxytitaniums has previously been extensively used by our group. We call the technique used the pulse-heating method. It has proven to be reliable for compounds that decompose significantly near their critical temperatures. In comparison with the other modern techniques applicable to thermally unstable compounds,^{8–10} the pulse-heating method provides much lesser residence times. By now the critical properties of about 170 substances have been measured using the pulse-heating method.

The method is based on the phenomenon of liquid superheat.^{11–13} In the course of the experiments, the pressure dependence of the temperature of the attainable superheat (spontaneous boiling-up) of liquid is measured. The critical point is not only the end point on the vapor–liquid equilibrium line, but the end point on the line of the attainable superheat as well. Thus, when the pressure in the liquid approaches the critical pressure, the temperature of the attainable superheat approaches the critical temperature.

The pulse-heating apparatus and procedure have been described in detail in previous publications.^{14–16} The block diagram of the apparatus is shown in Figure 1. A liquid under study filled a thin-walled Teflon cup. The pressure outside the cup was created by a press and measured by a dial gauge. The full-scale reading of the gauge was close to the critical pressure of the substance under study. The maximum uncertainty of the gauge was 0.15 % of the full-scale reading. Special experiments showed that the pressure drop on the cup walls did not exceed 0.02 MPa. 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 served simultaneously as a heater and a temperature element. The probe was included in a low-inductance bridge consisting of three branches. Square potential pulses were applied to the bridge from a generator. During a pulse the probe was heated. The amplitude of the pulse was adjusted in such a way that by the end of it the probe and the thin liquid layer near it were heated to the temperature of spontaneous boiling-up (attainable superheat).

The time from the start of a pulse to the moment of boiling-up was from (0.03 to 1.0) ms. At the moment of boiling-up a probe temperature perturbation arises from an abrupt change of the conditions of heat transfer from the probe to the liquid. The temperature perturbation is uniquely connected with a voltage perturbation on the probe. This perturbation was isolated with the help of an amplifying filter with a controllable bandwidth. Then the signal which we called the boiling signal was observed on the screens of a digital oscilloscope and a personal computer. The bridge was adjusted with a resistance box R_2 in such a way that its balance corresponded to the beginning of the boiling signal. For an exact fixation of the moment of balance one made use of a potential difference comparator, which at that moment gave a potential step that was also observed on the oscilloscope and the personal computer. The sensitivity of the comparator was 4 mV; the time delay was 100 ns. The temperature of the probe at the moment of boiling-up was determined from the condition of the bridge balance and by the well-known temperature dependence of the resistance of platinum. The temperature determined in such a way was the probe-volume average, whereas boiling-up took place on the surface of the probe in its middle part. The temperature of boiling-up (attainable superheat) was calculated taking into account the thermal losses at the probe ends and the radial inhomogeneity of the temperature field.

If the compound under study was liquid at room temperature, the measuring chamber also was at room temperature. If the melting point of the compound under investigation was higher than room temperature, the chamber was at a temperature of (10 to 15) K above the melting temperature. For this purpose, there were a furnace and a temperature control system in the apparatus, which maintained the temperature of the compound under study within ± 1 K. Such a precision was enough.

When the measuring chamber was filled with a liquid under study, the pressure established in it was somewhat higher than the atmospheric pressure. The pulses from the generator were periodically applied to the probe. The amplitude of the pulses was increased until the boiling signal was observed on the oscilloscope screen. By changing the box resistance from pulse to pulse the potential step from the comparator was brought into coincidence with the beginning of the boiling signal. The temperature of the attainable superheat at a given pressure was measured in such a way. As an

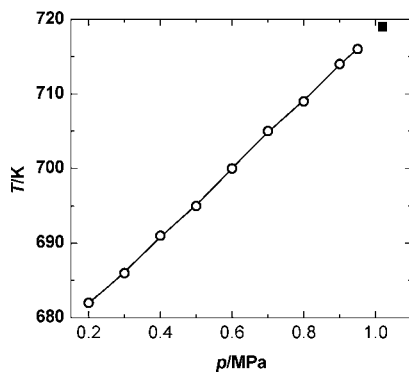


Figure 2. Temperature of the attainable superheat of tetrabutoxytitanium (○) vs the pressure; ■, critical point.

example, the results of the measurement of the temperature of the attainable superheat for tetrabutoxytitanium are given in Figure 2. The probe temperature perturbation in the initial stage of boiling-up may be both positive and negative. The sign of the perturbation is determined by the competition of two effects. A vapor bubble growing on the probe screens a part of the probe surface, which leads to a more rapid increase of the probe temperature (positive temperature perturbation). On the other hand, a growing bubble consumes heat for evaporation, which causes a negative temperature perturbation. Our large experience showed that for comparatively low-molar-mass compounds (nonpolymers) at near-critical pressures the temperature perturbation was negative. As the pressure approaches the critical pressure, the properties of the liquid and vapor phases come closer, and the amplitude of the temperature perturbation decreases.

The pressure in the liquid increased step by step until the negative temperature perturbation dropped to the level of the apparatus sensitivity ($1 \cdot 10^{-3}$ K). The last circle in Figure 2 ($p = 0.95$ MPa, $T = 716$ K) corresponds to this condition. 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 connected with the peculiarities of bubble nucleation and the growth of vapor bubbles near the measuring probe.

The true critical constants of a stable compound were calculated from the following equations:

$$p_c = p_c^m / \pi_0 \quad T_c = T_c^m / \tau_0 \quad (1)$$

where $1/\pi_0$ and $1/\tau_0$ are correction factors.¹⁴ 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.¹⁷ The formulas contain the acentric factor of the compound under study:¹⁸

$$\omega = -1 - \log_{10} \left(\frac{p_{vp}(T/T_c = 0.7)}{p_c} \right)$$

where p_{vp} is the vapor pressure. The acentric factors and the critical properties of tetraalkoxytitaniums 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 compounds under study at $T/T_c = 0.7$ was estimated by the following equation:¹⁹

$$\ln p_{vp} = B - \frac{C}{T^{1.30}} \quad (2)$$

The parameters B and C were calculated from the values of p_c^m and T_c^m and the boiling temperature measurements at reduced pressures collected by Bradley and co-workers.⁴ Using the degree of 1.30 in eq 2 instead of the usually used 1.0 provides a better accuracy of the estimation of the acentric factors. Then the values of π_0 and τ_0 and, using eq 1, p_c and T_c were calculated. For the second iteration, the acentric factor and the critical temperature and pressure of tetraalkoxytitaniums 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 the acentric factor.

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 the compound under investigation. The factor G_T was measured in one experiment with the critical constants as described previously¹⁴ and estimated at 1.5 K^{-1} . The ideal gas heat capacity was estimated using the atomic contribution method by Harrison and Seaton.²⁰

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 tetraalkoxytitaniums were measured with the help of probes of (1, 2, and 3) cm in length at heating times $t^* = (0.03, 0.06,$

Table 2. Critical Temperatures and Pressures of Tetraalkoxytitaniums: Experimental Values and Comparison with Predictive Methods

compound	T_c			p_c			
	exptl	ref 28	ref 29	exptl	ref 26	ref 28	ref 29
tetraethoxytitanium	647 ± 6	607.7	584.3	1.40 ± 0.04	2.234	1.551	1.299
tetrapropoxytitanium	685 ± 7	679.6	666.4	1.15 ± 0.04	1.691	1.190	1.134
tetrabutoxytitanium	719 ± 7	731.0	726.8	1.02 ± 0.03	1.427	0.952	1.021
tetrapentoxytitanium	751 ± 8	771.0	774.7	0.91 ± 0.03	1.234	0.786	0.941
tetrahexoxytitanium	780 ± 8	803.7	814.3	0.78 ± 0.02	1.087	0.666	0.881
tetraheptoxytitanium	808 ± 8	831.4	848.1	0.73 ± 0.02	0.972	0.576	0.836
tetraoctoxytitanium	831 ± 8	855.4	877.7	0.66 ± 0.02	0.878	0.508	0.801
tetranonoxytitanium	855 ± 9	876.6	903.8	0.63 ± 0.02	0.801	0.454	0.773
tetradecoxytitanium	882 ± 9	895.6	927.3	0.61 ± 0.02	0.737	0.411	0.750
AAPE/% ^a		2.7	4.7		37.3	14.1	10.1
MAPE/% ^b		6.1	9.7		59.6	32.6	23.0

^a AAPE = $(1/N)(\sum |Y_c^{\text{exp}} - Y_c^{\text{calc}}|/Y_c^{\text{exp}})$, where N is the number of experimental data points, Y_c^{exp} is the experimental value of the critical property, and Y_c^{calc} is the calculated value of the critical property. ^b MAPE = $(|Y_c^{\text{exp}} - Y_c^{\text{calc}}|_{\text{max}}/Y_c^{\text{exp}})$.

0.11, 0.22, and 0.46) ms. Two to five samples of each compound were used in the experiments. The tetraalkoxytitaniums investigated by us are unstable at their critical points. However, in our experiments they 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 of the probe lengths, heating times, and samples.

The coordinates of the true critical point of tetrabutoxytitanium shown in Figure 2 were calculated as described above. For this compound the correction factors were the following: $1/\pi_0 = 1.074$ and $1/\tau_0 = 1.005$.

Uncertainties. The uncertainties of the critical constants measured by the pulse-heating method were discussed in detail in our previous papers.^{21,22} In the course of our experiments the tetraalkoxytitaniums studied behaved like stable substances. For stable compounds the uncertainties of the results of measuring the critical pressure and temperature may be written as follows:

$$\begin{aligned}\delta p_c &= \delta p_{c1} + \delta p_{c2} + \delta p_{c3} \\ \delta T_c &= \delta T_{c1} + \delta T_{c2} + \delta T_{c3}\end{aligned}$$

Here δp_{c1} is the uncertainty with which an experimenter determines the pressure at which the temperature perturbation decreases to the level of the apparatus sensitivity, δp_{c2} the uncertainty of measuring this pressure with a dial gauge, and δp_{c3} the uncertainty of calculating the correction factor $1/\pi_0$. The uncertainty δT_{c1} has the same nature as δp_{c1} ; δT_{c2} is the uncertainty of measuring the probe temperature from its resistance, and δT_{c3} is the uncertainty of estimating the correction factor $1/\tau_0$. The uncertainties δp_{c1} and δT_{c1} can be reduced by repeated experiments to the values $0.01p_c^m$ and $0.001T_c^m$. The uncertainties δp_{c2} and δT_{c2} depend on the equipment used and for the experiments with tetraalkoxytitaniums are evaluated by us to about $0.0015p_c^m$ and $0.007T_c^m$. The uncertainties of calculating the correction factors are not easy to estimate because the formulas for their calculation were obtained by solving a rather complex thermophysical problem.²³ By now using the pulse-heating method we have measured the critical properties of about 170 compounds of different chemical natures. Among these compounds, there are those whose critical constants have been well-investigated. These are *n*-alkanes, naphthalene, water, some alkylbenzenes, alkanolic acids, alkylcyclohexanes, *n*-diaminoalkanes, siloxanes, and so forth. Our great experience allows us to estimate the values of $\delta p_{c3} \approx 0.02p_c$, and $\delta T_{c3} \approx 0.002T_c$; for compounds with hydrogen bonding or with high acentric factors ($\omega \geq 1$), $\delta p_{c3} \approx 0.03p_c$, and $\delta T_{c3} \approx 0.007T_c$. We estimate the uncertainties for tetraalkoxytitaniums studied at $0.03 p_c$ and $0.01 T_c$, where T_c is the absolute temperature. It corresponds to uncertainties from (± 0.04 to ± 0.02) MPa for the critical pressure and from (± 7 to ± 9) K for the critical temperature.

Results and Discussion

The critical temperatures and pressures of tetraalkoxytitaniums studied in this work are given in Table 2 and Figure 3. To our knowledge, the critical properties of these compounds have never been measured before. There are several ways to check the internal consistency of the data obtained. The first way is connected with the well-known correlation by Lydersen as presented by Reid et al.,²⁴ which predicts that the quantity $(M/p_c)^{1/2}$ should be a linear function

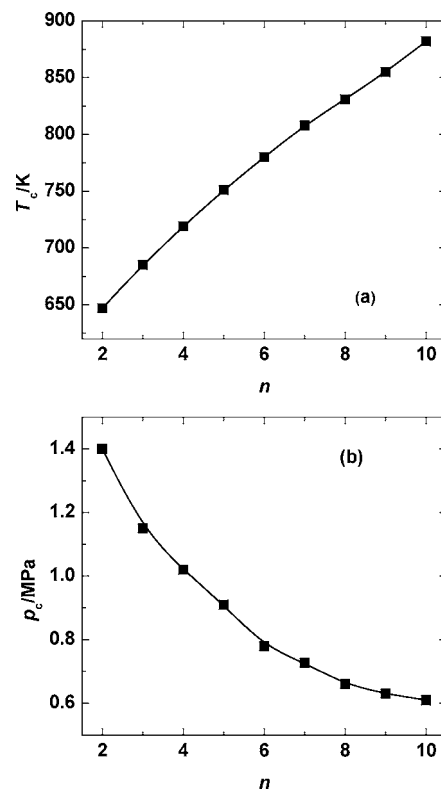


Figure 3. Critical temperatures (a) and pressures (b) of tetraalkoxytitaniums $\text{Ti}[\text{O}(\text{CH}_2)_n\text{H}]_4$ vs the number of CH_2 groups n in the alkyl radical.

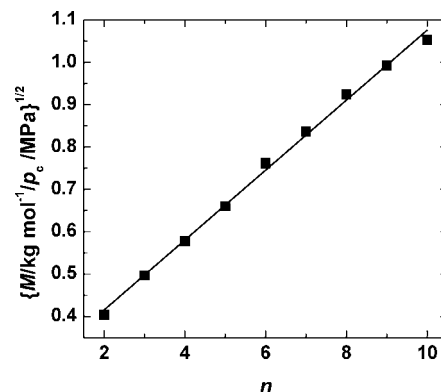


Figure 4. Correlation of the critical pressure of tetraalkoxytitaniums $\text{Ti}[\text{O}(\text{CH}_2)_n\text{H}]_4$ as a function of the number of CH_2 groups n in the alkyl radical and molar mass M .

of the number of CH_2 groups in a molecule for a given homologous series. Here M is the molar mass. The critical pressures of tetraalkoxytitaniums measured by us follow this rule well enough. The solid line in Figure 4 corresponds to the following equation:

$$\{[M/(\text{kg} \cdot \text{mol}^{-1})]/[p_c/\text{MPa}]\}^{1/2} = 0.2496 + 0.0826n$$

The quantity T_c/p_c is also a linear function of the number of CH_2 groups in a molecule²⁵ at least for compounds of moderate molar mass. The result of the correlation of the ratio T_c/p_c with the number of CH_2 groups in the alkyl radical of a molecule of a tetraalkoxytitaniums is given in Figure 5. The solid line corresponds to the equation:

$$(T_c/\text{K})/(p_c/\text{MPa}) = 174.47 + 134.25n$$

Figures 4 and 5 prove the good internal consistency of our experimental data.

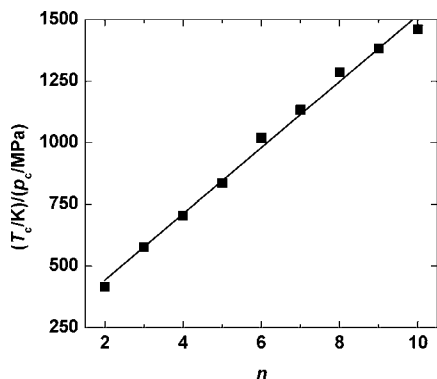


Figure 5. Ratio of the critical temperature to the critical pressure of tetraalkoxytitaniums $\text{Ti}[\text{O}(\text{CH}_2)_n\text{H}]_4$ against the number of CH_2 groups n in the alkyl radical.

Table 3. Contribution of Titanium(IV) for the Calculation of the Critical Temperature and Critical Pressure in the Methods of Constantinou and Gani²⁸ and Marrero and Gani²⁹

property	ref 28	ref 29
T_c	-2.3505	-4.1761
p_c	0.025550	0.122630

We know two methods for estimating the critical constants of compounds whose molecules contain titanium. The method suggested by Somayajulu²⁶ requires the normal boiling point for the estimation of the critical temperature. In the method of Wilson and Jasperson as presented by Poling et al.²⁷ the normal boiling temperature is used for the calculation of both the critical temperature and the critical pressure. We have already pointed out that the data on the normal boiling points that could sometimes be found in the literature were not reliable because of the decomposition of alkoxytitaniums. Thus, using these two methods we can calculate only the critical pressures of alkoxytitaniums. However, Table 2 shows that the method of Somayajulu considerably overestimates the critical pressure of tetraalkoxytitaniums.

Because of this we took the well-known group contribution methods of Constantinou and Gani²⁸ and Marrero and Gani²⁹ and calculated the contributions of titanium using our experimental data. These contributions are shown in Table 3. The contributions are based on a small amount of experimental data and should be corrected as new results of the measurements of the critical properties appear. The critical temperatures and pressures of tetraalkoxytitaniums estimated in such a way are given in Table 2. Both of the methods predict a stronger growth of the critical temperature with increasing number of CH_2 groups in a molecule of tetraalkoxytitaniums than the experiment gives. The average absolute percent error (AAPE) is 2.7 % and 4.7 % for the methods of Constantinou and Gani²⁸ and Marrero and Gani²⁹ respectively. The critical pressures of tetraalkoxytitaniums are estimated by the methods of Constantinou and Gani and Marrero and Gani with the contributions determined by us being much worse than the critical temperatures. The values of AAPE are equal to 14.1 % (the method of Constantinou and Gani) and 10.1 % (that of Marrero and Gani).

Conclusion

The critical pressures and temperatures of tetraalkoxytitaniums $\text{Ti}[\text{O}(\text{CH}_2)_n\text{H}]_4$ with $n = 2$ to 10 have been measured. The correlation of the quantities $(M/p_c)^{1/2}$ and T_c/p_c with the number of CH_2 groups n in the molecules of tetraalkoxytitaniums has shown good internal consistency of the experimental data

obtained. The contributions of a titanium(IV) atom in the group contribution methods of Constantinou and Gani and Marrero and Gani have been calculated from the experimental data. Using these contributions, the critical pressures and temperatures of tetraalkoxytitaniums have been estimated by these methods. For the critical temperature, the AAPE is 2.7 % and 4.7 % for the methods of Constantinou and Gani and Marrero and Gani, respectively. For the critical pressure, the values of AAPE are equal to 14.1 % (the method of Constantinou and Gani) and 10.1 % (that of Marrero and Gani).

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