Critical Point Measurements for Five *n*-Alkylcyclohexanes (C_6 to C_{10}) by the Pulse-Heating Method

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This paper presents experimental critical temperatures and pressures of five *n*-alkylcyclohexanes $C_6H_{11}C_nH_{2n+1}$ with the number of carbons in the side chain $n = 0, 1, 2, 3$, or 4. The method of pulse heating of a wire probe immersed into the liquid under study has been used. Residence times are from (0.01 to 1) ms. Equations for the correlation of the critical temperatures and pressures of *n*-alkylcyclohexanes with the number of carbon atoms in the side chain, normal boiling point, and molar mass have been obtained. The experimental critical constants of alkylcyclohexanes have been compared with the values calculated by the group-contribution methods of Lydersen, Joback and Reid, and Constantinou and Gani.

Introduction

This paper is part of our investigation on the effect of various end groups on the critical properties of substances consisting of chain molecules. Previously we have measured the critical constants of normal alkanes,[1] 1-alkanols,[2] alk-1-enes,[3] alkanoic acids,[4] and 1-phenylalkanes.[5] In this paper we report the measurements of the critical temperatures and pressures of five alkylcyclohexanes (C_6 to C_{10}) made by the pulse-heating method.

Experimental Section

Method. The pulse-heating apparatus and procedures used in this study have been described in detail previously.[2,6,7] The minimum of the experimental details is given below. The pulse-heating method consists of measuring the pressure dependence of the temperature of the attainable superheat (spontaneous boiling-up). With increasing pressure, the temperature of the attainable superheat tends to the critical temperature. The liquid under study fills the chamber, the pressure in which is measured by a dial gauge. A platinum wire probe, 2×10^{-3} cm in diameter and (1 to 3) cm in length, is immersed in the liquid. It is heated by rectangular pulses of electric current. By the end of a pulse the probe and the thin liquid layer that surrounds it are heated to the temperature of spontaneous boiling-up. The amplitude of pulses is chosen in such a way that the time from the start of a pulse to the moment of boiling-up is from (0.01 to 1.0) ms. At the moment of boiling-up, the conditions of heat transfer from the probe to the liquid change abruptly against the background of a smooth temperature increase and a temperature perturbation caused by boiling-up takes place. The probe temperature at this moment is determined from its resistance. The pressure in the chamber increases step by step until the negative temperature perturbation decreases to the level of the apparatus sensitivity for this parameter (1×10^{-3} K). This pressure is 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 is taken to be equal to the measured value of the critical temperature T_c^m.

One can suggest that the amplitude of the temperature perturbation approaches zero at the critical point. Because the apparatus sensitivity is finite (nonzero), the measured values of the critical pressure and temperature are always smaller than the critical ones. The true critical pressure p_c and critical temperature T_c of a compound under study are calculated by the following equation:

$$p_c = p_c^m/\pi_0, \quad T_c = T_c^m/\tau_0 \tag{1}$$

where p_c^m and T_c^m are the measured values of the critical pressure and temperature, respectively, and $1/\pi_0$ and $1/\tau_0$ are the correction factors.[6,8] For the cyclohexanes investigated, the correction factors vary from $\pi_0 = 0.9911$, $\tau_0 = 0.9990$ (cyclohexane) to $\pi_0 = 0.9764$, $\tau_0 = 0.9978$ (butylcyclohexane). In calculating these correction factors, the thermophysical properties of the substance under investigation near the critical point are required, which are estimated using the principle of corresponding states. The appropriate formulas are given in our previous paper.[8] To use them, it is necessary to know the acentric factor of the liquid under study. The acentric factors of *n*-alkylcyclohexanes were estimated in the following way. The acentric factors of cyclohexane and methylcyclohexane were calculated using the critical properties recommended by Daubert[9] and the vapor pressures given by Vargaftik.[10] The acentric factors and the critical constants of the other alkylcyclohexanes were calculated by an iteration method. At first, as the critical constants, we used p_c^m and T_c^m; the vapor pressures were estimated using the Clapeyron equation and the normal boiling points taken in accordance with the TRC recommendations.[11] This is a rough estimation, but the values of π_0 and τ_0 are not very sensitive to variations in the acentric factor ω. For instance, for cyclohexane, a change of 10% in ω causes a change of about 0.05% in p_c and 0.01% in T_c. Then we calculated π_0 and τ_0 and by eq 1 p_c and T_c. For the second iteration, the acentric factors and the critical properties were calculated using corresponding values after the first iteration. Two iterations were enough, for, as discussed above, the values of π_0 and τ_0 are little affected by variations of acentric factors.

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Table 1. Purity of Materials Used in Critical Point Measurements

compound	supplier	purity/%	
		supplier	real[a]
cyclohexane	Fluka	99.5	99.2
methylcyclohexane	Aldrich	99	99.6
ethylcyclohexane	Fluka	>99	99.5
propylcyclohexane	Aldrich	99	99.7
butylcyclohexane	Aldrich	99+	99.6

[a] The average between the values determined before and after measuring the critical properties.

The ideal gas capacity was also used in calculating the correction factors. It was calculated by the method of Rihani and Doraiswamy as presented by Reid et al.[12] The formulas for calculating the correction factors contain the factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation. This factor was measured together with the critical constants in one experiment and was estimated at 1.5 K^{-1}.

The critical temperature T_c and pressure p_c of a thermally unstable substance determined in such a way 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 true values of the critical constants of a thermally unstable substance are determined then by extrapolation of T_c and p_c as functions of t^* to $t^* = 0$, as described in refs 6 and 13. We failed to find in the literature any data about the thermal stability of alkylcyclohexanes in the liquid phase. The well-known studies on the pyrolysis of cyclohexanes deal with the vapor phase and temperatures that are much higher than the critical ones.[14,15] One can presume that the thermal stability of alkylcyclohexanes is close to that of linear alkanes. Normal alkanes are known to begin decomposing in the critical point measurements at about 640 K.[16] Then alkylcyclohexanes from cyclohexane to propylcyclohexane are likely to be stable at their critical points, and only butylcyclohexane is, perhaps, mildly unstable. In any case, we could detect no change of the critical temperature or pressure under variation of t^*, and the procedure of extrapolation was not used.

Sources and Purities of the Substances Studied. The sources and purities of cyclohexanes are given in Table 1. Before and after measuring the critical constants, the purities were verified by gas chromatography (Shimadzu GS-Ha). The samples analyzed after the measurements of the critical properties had lower purities; the concentration of the main substance fell by from (0.05 to 0.43)%.

Uncertainties. The uncertainties of the results of measuring the critical pressures and temperatures by the pulse-heating method were discussed in detail in our previous paper.[5] The main problem here is to estimate the uncertainties of calculating the correction factors $1/\pi_0$ and $1/\tau_0$. The comparison of the critical constants obtained by the pulse-heating method with the literature values for well-studied substances shows that, as a rule, the pulse-heating method underestimates the critical temperature and pressure. It indicates that the true correction factors should be greater than the values given by the formulas we used.[6] They were obtained by solving a complex thermophysical problem in the course of which we had to make some assumptions. In this situation, the uncertainties were determined by comparing the literature values of the critical constants of some "standard" substances (pentane, hexane, heptane, water, and naphthalene) with those obtained by the pulse-heating method. In addition, in this work we measured the critical pressures and temperatures of cyclohexane and methylcyclohexane (see Tables 2 and 3). These compounds are well investigated.[9] For all these substances the difference between the literature and our data does not exceed $0.01T_c$ and $0.03p_c$. We consider these values as the uncertainties.

Table 2. Critical Temperatures of *n*-Alkylcyclohexanes $C_6H_{11}C_nH_{2n+1}$: Experimental Values and Comparison with Predictive Methods (T_b Is the Normal Boiling Point)

				T_c/K		
n	T_b[a]/K	T_c/K	$\pm\delta T_c$/K	ref 12	ref 17	ref 18
0	353.9	553.8[b]	0.2	553.83	554.36	558.22
		551[c]	6			
1	374.0	572.1[b]	0.2	571.35	573.79	575.78
		569[c]	6			
2	405	604[c]	6	604.20	607.37	613.79
3	429	624[c]	6	626.07	629.87	633.97
4	453	650[c]	6	647.74	652.12	652.12
AAPE[d]/%				0.17	0.26	1.00

[a] According to the TRC recommendation.[11] [b] According to Daubert.[9] [c] This work. [d] AAPE = average absolute percent error; AAPE/% = $1/N\Sigma((|T_c^{exp} - T_c^{cal}|)/T_c^{exp}) \times 100\%$, where N is the number of experimental data points, T_c^{exp} is the experimental value of the critical temperature, and T_c^{cal} is the calculated value of the critical temperature.

Table 3. Critical Pressures of *n*-Alkylcyclohexanes $C_6H_{11}C_nH_{2n+1}$: Experimental Values and Comparison with Predictive Methods

			P_c/MPa		
n	p_c/MPa	$\pm\delta p_c$/MPa	ref 12	ref 17	ref 18
0	4.08[a]	0.03	4.017	4.130	3.774
	4.06[b]	0.12			
1	3.48[a]	0.02	3.438	3.522	3.348
	3.47[b]	0.10			
2	3.25[b]	0.10	3.048	3.153	3.075
3	2.86[b]	0.09	2.738	2.838	2.765
4	2.56[b]	0.08	2.486	2.569	2.502
AAPE[c]/%			2.65	1.31	4.45

[a] According to Daubert.[9] [b] This work. [c] AAPE = average absolute percent error; AAPE/% = $1/N\Sigma((|p_c^{exp} - p_c^{cal}|)/p_c^{exp}) \times 100\%$, where N is the number of experimental data points, p_c^{exp} is the experimental value of the critical pressure, and p_c^{cal} is the calculated value of the critical pressure.

Results and Discussion

The critical pressures and the critical temperatures of *n*-alkylcyclohexanes from cyclohexane to butylcyclohexane measured in this work are given in Tables 2 and 3 together with their uncertainties. These tables contain the values recommended by Daubert[9] for cyclohexane and methylcyclohexane as well. The critical temperatures and pressures of alkylcyclohexanes were also estimated by the well-known group-contribution methods of Lydersen,[12] Joback and Reid,[17] and Constantinou and Gani.[18] The Lydersen and Joback and Reid methods require knowledge of the normal boiling point (T_b) for the estimation of the critical temperature. Normal boiling points for the cyclohexanes studied were taken in accordance with the TRC recommendations.[11]

Table 2 shows that for alkylcyclohexanes the Lydersen method gives the best results. The method of Joback and Reid and especially that of Constantinou and Gani, in general, overestimate the critical temperatures. For the critical pressures (Table 3), the method of Joback and Reid is the best; the methods of Lydersen and Constantinou and Gani underestimate the critical pressures of cyclohexanes.

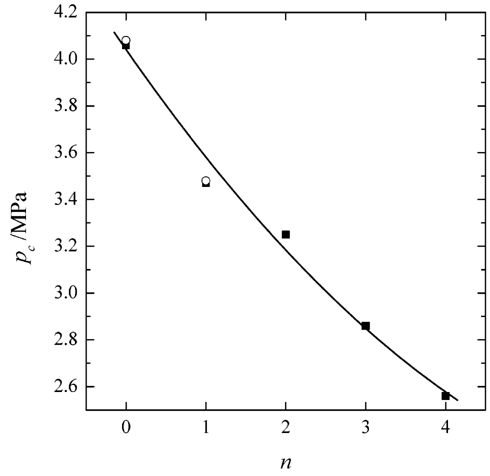

Figure 1. Critical pressures of *n*-alkylcyclohexanes vs the number of carbon atoms in the side chain: ○, ref 9; ■, this work.

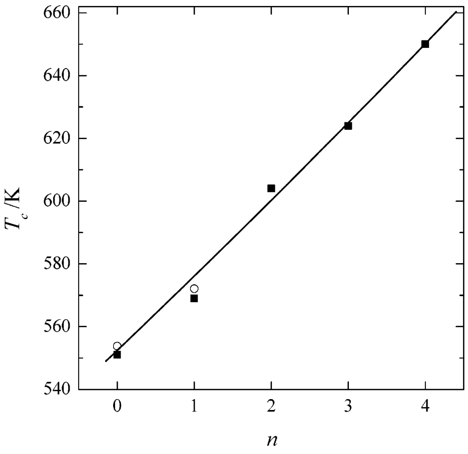

Figure 2. Critical temperatures of *n*-alkylcyclohexanes vs the number of carbon atoms in the side chain: ○, ref 9; ■, this work.

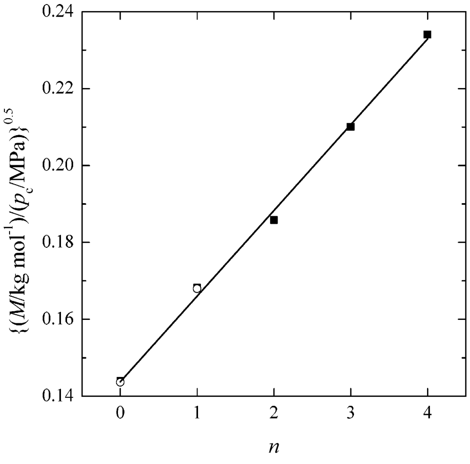

Figure 3. Correlation of the critical pressure of *n*-alkylcyclohexanes as a function of the number of carbon atoms in the side chain and molar mass. Critical pressures: ○, ref 9; ■, this work; the solid line corresponds to eq 2.

The self-consistency of the data obtained was examined by evaluating four plots: p_c versus *n* (Figure 1), T_c versus *n* (Figure 2), $(M/p_c)^{0.5}$ versus *n* (Figure 3), and (T_c/T_b) versus *n* (Figure 4), where *n* is the number of carbons in the side chain of the alkylcyclohexane and *M* is the molar mass. The solid lines in Figures 3 and 4 correspond to the following equations ($0 \leq n \leq 4$):

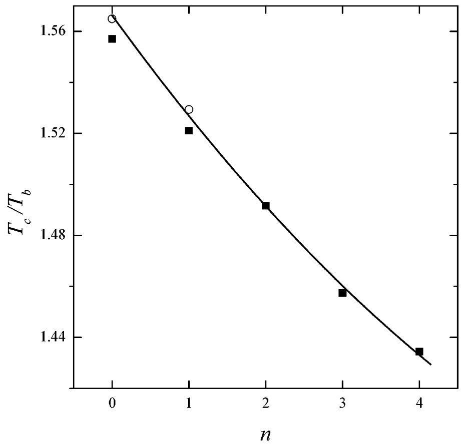

Figure 4. Correlation of the critical temperature of *n*-cyclohexanes as a function of the number of carbon atoms in the side chain and normal boiling point. Critical temperatures: ○, ref 9; ■, this work; the solid line corresponds to eq 3.

$$\{(M/\text{kg}\cdot\text{mol}^{-1})/(p_c/\text{MPa})\}^{0.5} = 0.14371 + 0.0223n \tag{2}$$

$$\frac{T_c}{T_b} = 1.56621 - 0.04147n + 0.00205n^2 \tag{3}$$

The solid lines in Figures 1 and 2 correspond to polynomials of the second order and are used only for smoothing the data. We do not give them here because they do not have a great physical meaning. To obtain these polynomials and eqs 2 and 3, we used the critical temperatures and pressures recommended by Daubert[9] for cyclohexane and methylcyclohexane and our data for the rest.

Conclusion

The critical pressures and temperatures of five *n*-alkylcyclohexanes have been measured by the pulse-heating technique. Our data for cyclohexane and methylcyclohexane are in good agreement with the values recommended by Daubert.[9] The critical constants have been correlated with the number of carbons in the side chain of alkylcyclohexane, the molar mass, and the normal boiling point.

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