Critical-Point Measurements for Phenylethanoic to 7-Phenylheptanoic Acids

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The critical temperatures and pressures of phenylalkanoic acids with a straight alkyl chain $C_6H_5(CH_2)_nCOOH$ (n = 1 to 6) have been measured. The method of pulse heating of a wire probe placed into the substance under study has been used. The method minimizes the thermal decomposition because residence times are from (0.035 to 1) ms. An equation for the correlation of the critical pressures of phenylalkanoic acids with the number of CH_2 groups between phenyl and carboxyl functional groups and molar mass has been obtained. The experimental critical constants of phenylalkanoic acids have been compared with the values calculated by the group-contribution methods of Constantinou and Gani and Marrero and Gani.

Introduction

Phenylalkanoic acids with a straight alkyl chain $C_6H_5(CH_2)_n$-COOH are an important group of organic acids. However, the experimental critical properties of phenylalkanoic acids are unknown. They are difficult to measure because these acids decompose before attaining their critical states. In this article, we report the experimental critical temperatures and pressures for six phenylalkanoic acids from phenylethanoic to 7-phenylheptanoic acid using the pulse-heating method applicable to thermally unstable substances.

Experimental Section

Method. The pulse-heating method is based on measuring the pressure dependence of the temperature of the attainable superheat (spontaneous boil-up) of a liquid with the help of a thin wire probe heated by pulses of electric current with a duration from (0.01 to 1.0) ms. With increasing pressure, the temperature of the attainable superheat tends to the critical temperature. The pulse-heating apparatus and procedures that were used have been described in detail previously.[1−3]

A study of well-investigated substances has shown that the values of the critical pressure p_c^m and the critical temperature T_c^m obtained in the course of pulse-heating experiments are, as a rule, lower than most reliable literature values. According to the model of boil-up of a liquid at the surface of the probe,[4] the true critical pressure p_c and critical temperature T_c of a stable compound are calculated by the following equations

$$p_c = \frac{p_c^m}{\pi_0} \qquad T_c = \frac{T_c^m}{\tau_0} \tag{1}$$

where $1/\pi_0$ and $1/\tau_0$ are the correction factors.[1,5] For the phenylalkanoic acids studied, the correction factors vary from $1/\pi_0 = 1.039$, $1/\tau_0 = 1.003$ (phenylethanoic acid) to $1/\pi_0 = 1.074$, $1/\tau_0 = 1.004$ (7-phenylheptanoic acid). To calculate the correction factors, the thermophysical properties of the substance under investigation near the critical point are used. They are estimated using the principle of corresponding states, which requires a knowledge of the acentric factor of the liquid under study. The acentric factors and the critical constants of the phenylalkanoic acids were calculated by an iteration method. At first as the critical constants, we took p_c^m and T_c^m; the vapor pressures of phenylethanoic and 3-phenylpropanoic acids were calculated using the Antoine equation with parameters taken from the NIST Chemistry WebBook.[6] The vapor pressures of the rest of the aromatic acids were estimated by the following equation:

$$\ln p_{vp} = B - \frac{C}{T} \tag{2}$$

Parameters B and C were determined from the values of p_c^m and T_c^m and normal and reduced boiling points also taken from the NIST Chemistry WebBook[6] and in accordance with the Alfa Aesar recommendations[7] (for 7-phenylheptanoic acid). The acentric factors obtained in such a way showed large scattering; the smoothed values of the acentric factor ω were estimated using the equation suggested by us in a previous paper:[8]

$$\omega = a + bn^{2/3} \tag{3}$$

Here, n is the number of CH_2 groups in an acid molecule. Then we calculated π_0 and τ_0 and, from 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 the values of π_0 and τ_0 , which are affected very little by variations in acentric factors. For instance, for phenylethanoic acid a change of 20 % in the acentric factor produces a change of about 0.3 % in π_0 and, consequently, in the critical pressure and 10^{-4} % in τ_0 and the critical temperature. Therefore, even a rough evaluation of the

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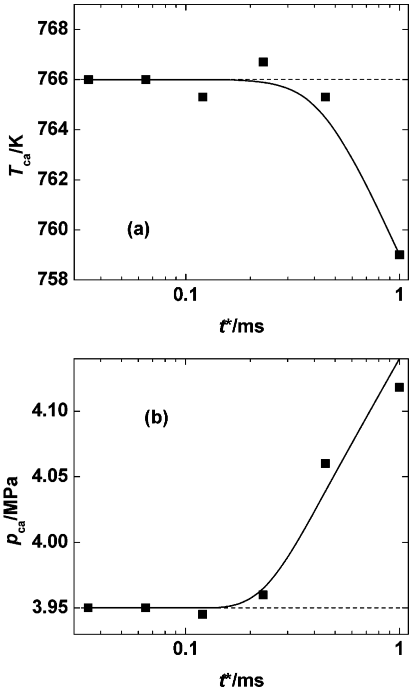

Figure 1. Apparent critical temperature (a) and critical pressure (b) of phenylethanoic acid in pulse-heating experiments; t* is the time from the beginning of a heating pulse to the moment of boil-up. The dashed lines correspond to averaging the experimental values for heating times from (0.035 to 0.23) ms.

thermophysical properties of a compound under study gives an estimation of the correction factors with tolerable uncertainties.[9]

In the calculation of the correction factors, the ideal gas capacity was also used. It was estimated using the method of Rihani and Doraiswamy as presented by Reid et al.[10] The formulas for calculating the correction factors contain the factor

$$G_T \equiv \frac{\partial \ln J}{\partial T} \qquad (4)$$

where J is the rate of bubble nucleation. This factor was measured together with the critical constants in one experiment and was estimated to be 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 boil-up t* due to the decomposition of a compound under study in the course of heating. The true values of the critical constants of an unstable compound are determined then by extrapolation of T_c and p_c as functions of t* to $t^* = 0$ as described in ref 11. However, we could not use this procedure because the kinetic parameters of the reaction of decomposition of the phenylalkanoic acids were unknown, so we applied a simplified procedure. The critical temperatures and pressures were measured with the help of probes that were (1, 2, and 3) cm in length at heating times $t^* = (0.035, 0.065, 0.12, 0.23, 0.45,$ and $1.00)$ ms. Several samples (from five to seven) of each compound were used. Figure 1 presents, as an example, the results of measuring the constants of phenylethanoic acid. The points in this figure are the result of averaging over all lengths and all samples. The critical constants of the compounds under investigation were determined by averaging the apparent critical constants over the heating times from (0.035 to 0.23) ms.

Sources and Purities of the Substances Studied. The sources and purities of phenylalkanoic acids are given in Table 1. Acids from phenylethanoic to 5-phenylpentanoic were purchased from Sigma-Aldrich Co; 6-phenylhexanoic and 7-phenylheptanoic acids were synthesized by Yu. Yatluk (the Institute of Organic Synthesis, Ural Branch of RAS, Ekaterinburg). These acids were obtained from cyclopentanone and cyclohexanone, respectively, using the Hunig reaction according to the method by McIntyre et al.[12] In the last stage, instead of reduction on Clemmensen that on Kijner was used.[13] The products were distilled in vacuo three times. The purities were verified by gas chromatography (Shimadzu GS-Ha) before and after measuring the critical constants. For this purpose, the acids were dissolved in methylene chloride. The samples analyzed after the measurements of the critical properties had lower purities; the concentration of the main substance fell by (0.05 to 0.43) %.

Table 1. Purity of Materials Used in Critical-Point Measurements

			purity %		
compound	CASRN	supplier	supplier	before[a]	after[a]
phenylethanoic acid	103-82-2	Aldrich	99	99.58	98.90
3-phenylpropanoic acid	501-52-0	Aldrich	99	99.71	97.68
4-phenylbutanoic acid	1821-12-1	Aldrich	99	99.63	98.45
5-phenylpentanoic acid	2270-20-4	Aldrich	99	99.85	98.52
6-phenylhexanoic acid	5581-75-9	IOS[b]		99.40	99.35
7-phenylheptanoic acid	40228-90-8	IOS[b]		99.95	99.95

[a] The values determined before and after measuring the critical properties. [b] Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia.

The use of the pulse-heating method for measuring the critical properties presumes that the electrical conductivity of a substance under study is low. Otherwise, the resistance and the temperature of the wire probe are measured with large errors. Besides, electrolysis of the substance occurs on the surface of the probe. The electrical conductivity of the samples of the phenylalkanoic acids was determined by Dr. Sergey Shkerin from the Institute of High-Temperature Electrochemistry (Ekaterinburg) with the help of the IM-6 impedance measurement unit produced by Zahner Electrik. The measurements were carried out at a frequency of electric current from $(2 \text{ to } 8 \times 10^5)$ Hz. No evident dependence of the electrical conductivity on frequency was found. The temperature of the samples during the measurement the electrical conductivity was about 20 K higher than their melting temperature, which corresponds to the conditions of the measurement of the critical properties. The electrical conductivity of the samples of the phenylalkanoic acids ranged from $(10^{-6} \text{ to } 10^{-5})\ \Omega^{-1}\cdot\text{m}^{-1}$, so it cannot interfere with measuring the critical properties.

Uncertainties. The uncertainties in the critical pressure and temperature measured by the pulse-heating method were discussed in detail in our latest paper.[9] We estimate the uncertainties for the phenylalkanoic acids studied at $0.01T_c$ and $0.035p_c$.

Results and Discussion

The critical temperatures and pressures of phenylalkanoic acids are given in Table 2 and in Figures 2 and 3. The critical pressures were correlated with the molar mass M and the number of CH_2 groups n $(1 \le n \le 6)$:

$$\left(\frac{M/\text{kg}\cdot\text{mol}^{-1}}{p_c/\text{MPa}}\right)^{1/2} = 0.1651 + 0.02077n \qquad (5)$$

The critical constants of phenylalkanoic acids were also estimated using the well-known group-contribution methods by Constantinou and Gani[14] and Marrero and Gani[15] (Table 2). We did not use methods that require a knowledge of the normal boiling point because this parameter was measured only for

Table 2. Critical Temperatures and Pressures of Phenylalkanoic Acids $C_6H_5(CH_2)_nCOOH$: Experimental and Predicted Values

	T_c/K			p_c/MPa		
n	exptl	ref 14	ref 15	exptl	ref 14	ref 15
1	766 ± 8	718.3	767.8	3.95 ± 0.14	3.965	3.929
2	776 ± 8	729.9	778.7	3.46 ± 0.12	3.510	3.464
3	783 ± 8	740.8	789.1	3.21 ± 0.11	3.131	3.089
4	790 ± 8	751.1	799.0	2.95 ± 0.10	2.813	2.784
5	794 ± 8	760.8	808.6	2.60 ± 0.09	2.543	2.531
6	798 ± 8	770.1	817.7	2.47 ± 0.09	2.312	2.320
	AAPE[a]/%	5.03	1.13		2.92	3.13
	MAPE[b]/%	6.23	2.47		6.40	6.07

[a] AAPE $= (1/N)(\Sigma|Y_c^{\mathrm{exptl}} - Y_c^{\mathrm{calcd}}|/Y_c^{\mathrm{exptl}}) \times 100$ %, 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. [b] MAPE $= (|Y_c^{\mathrm{exptl}} - Y_c^{\mathrm{calcd}}|_{\max}/Y_c^{\mathrm{exptl}}) \times 100$ %.

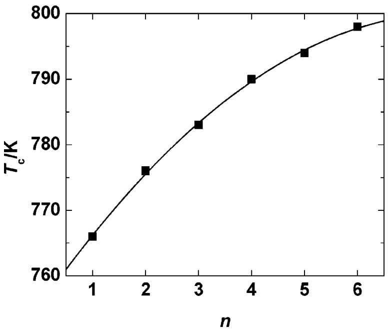

Figure 2. Critical temperatures of phenylalkanoic acids with straight alkyl chain $C_6H_5(CH_2)_nCOOH$ vs the number of CH_2 groups.

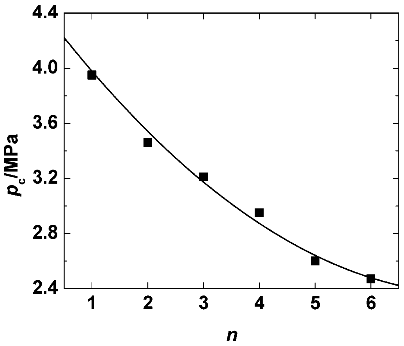

Figure 3. Critical pressures of phenylalkanoic acids with straight alkyl chain $C_6H_5(CH_2)_nCOOH$ vs the number of CH_2 groups.

phenylethanoic, 3-phenylpropanoic, and 4-phenylbutanoic acids.[6] The method of Constantinou and Gani considerably underestimates the critical temperatures of the phenylalkanoic acids studied whereas that of Marrero and Gani slightly overestimates them. For the critical temperatures evaluated using the method by Marrero and Gani, an average absolute error is close to the uncertainty of the measurements. However, the deviation of the calculated values from the experimental ones increases with increasing molar mass (Figure 5). For 7-phenylalkanoic acid, the deviation is approximately twice as large as the measurement uncertainty. It is good to bear this in mind when estimating the critical temperature of phenylalkanoic acids heavier than 7-phenylalkanoic acid. Both of these methods give similar values for the critical pressure and predict the critical pressures of the phenylalkanoic acids studied with an average absolute error that is close to the measurement uncertainty. The difference between experimental and predicted critical pressures probably has the tendency to increase (Figure 6), although this matter requires additional study.

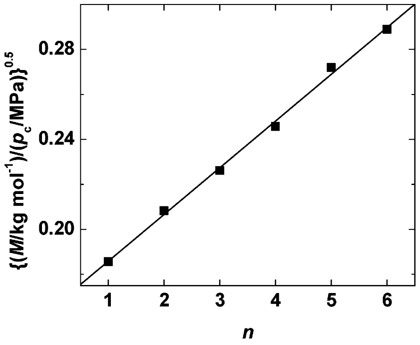

Figure 4. Correlation of the critical pressure of phenylalkanoic acids $C_6H_5(CH_2)_nCOOH$ with the number of CH_2 groups *n* and molar mass *M*.

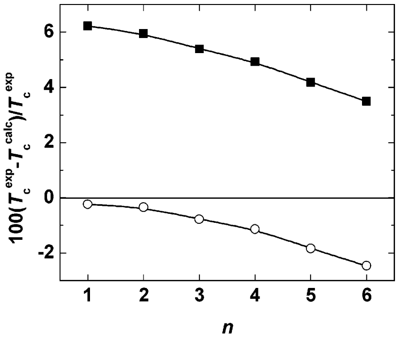

Figure 5. Percent deviations of the experimental critical temperatures from the values calculated by group-contribution methods as a function of the number of CH_2 groups in phenylalkanoic acids $C_6H_5(CH_2)_nCOOH$. GC methods: ■, Constantinou and Gani;[14] ○, Marrero and Gani.[15]

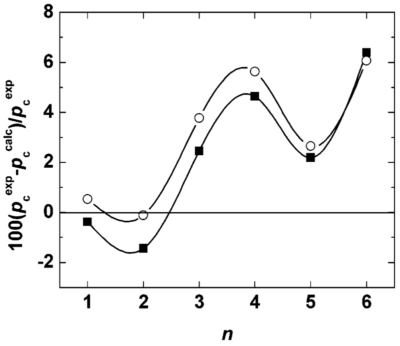

Figure 6. Percent deviations of the experimental critical pressures from the values calculated by group-contribution methods as a function of the number of CH_2 groups in phenylalkanoic acids $C_6H_5(CH_2)_nCOOH$. GC methods: ■, Constantinou and Gani;[14] ○, Marrero and Gani.[15]

Conclusions

The critical pressures and temperatures of six phenylalkanoic acids have been measured by the pulse-heating technique. Correlating the critical pressures with the number of CH_2 groups between phenyl and carboxyl functional groups in the acid molecule and the molar mass has shown the internal consistency of the data obtained. The method of Constantinou and Gani may be used to estimate the critical temperatures and pressures of phenylalkanoic acids. However, the deviation of calculated values from the experimental ones tends to be higher with increasing molar mass.

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