1336 *J. Chem. Eng. Data* **2007,** *52,* 1336−1339

Critical Point Measurements for *n*-Alkyl Benzoates (C_8 to C_{13})

Eugene D. Nikitin* and Alexander P. Popov

Institute of Thermal Physics, Ural Branch of Russian Academy of Sciences, Amundsena Street, 106, 620016 Ekaterinburg, Russia

Yuri G. Yatluk

Institute of Organic Synthesis, Ural Branch of Russian Academy of Sciences, Sof'i Kovalevskoi Street, 20, 620219 Ekaterinburg, Russia

The critical temperatures and critical pressures of six *n*-alkyl benzoates $C_6H_5COO(CH_2)_nH$ with $n = 1$ to 6 have been measured. All the substances are thermally unstable at their critical points. The method of pulse-heating of a wire probe placed into the liquid under study has been used. Residence times are from (0.03 to 1) ms, which results in little decomposition of the liquid in the course of measuring. The experimental critical properties of alkylbenzoates have been compared with the values estimated by the group contribution methods of Constantinou and Gani and Marrero and Gani.

Introduction

The paper reports the critical temperatures and pressures of the esters of benzoic acid with a straight alkyl chain $C_6H_5COO(CH_2)_nH$ from methyl benzoate ($n = 1$) to hexyl benzoate ($n = 6$). For methyl benzoate, the critical temperature and the critical density have been determined by Steele et al.[1] from differential scanning calorimetry results; sample decomposition was reduced by employing a single continuous heat at a heating rate of 0.333 $K \cdot s^{-1}$. Then, the critical pressure was derived from vapor pressure measurements. However, extensive sample decomposition precluded the achievement of near-critical temperatures for ethyl benzoate, and its critical properties were estimated from the measurement of vapor pressure and two-phase heat capacity. Therefore, it is reasonable to assume that all the benzoates studied by us are thermally unstable at their critical points. The pulse-heating method with ultralow residence times was used for our measurements.

Experimental Section

Materials. The samples of benzoates were of commercial origin and were used without further purification. The sources, purities, and Chemical Abstract Service Registry Numbers (CASRN) are given in Table 1. Before and after the measurements, the purities of the samples were determined by gas chromatography (Shimadzu GS-Ha) and proton magnetic spectroscopy (Bruker DRX 400). The purity of the samples is not significantly changed in the course of measuring the critical properties.

Table 1. Sources and Purities of Compounds Used in Critical Point Measurement

			purity/%				
			before measuring critical constants			after measuring critical constants	
compound	CASRN[a]	supplier	supplier[b]	GC	PMS	GC	PMS
methyl benzoate	93-58-3	Aldrich	>99.9	99.9	99.9	99.9	99.9
ethyl benzoate	93-89-0	Aldrich	99.9	99.9	99.9	99.9	99.9
propyl benzoate	2315-68-6	Aldrich	99.90	99.9	99.9	99.9	99.9
butyl benzoate	136-60-7	Aldrich	99.9	99.9	99.9	99.9	99.9
pentyl benzoate	2049-96-9	Alfa Aesar	99.6	99.0	99.2	99.0	99.1
hexyl benzoate	6789-88-4	Alfa Aesar	99.2	99.8	99.6	99.8	99.5

[a] Chemical Abstracts Service Registry Number. [b] For a given lot.

Method. The pulse-heating apparatus and procedures used for the measurements have been described in detail in previous publications.[2−4] A liquid under study filled a Teflon cup with thin walls, 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 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 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 dropped to the level of the apparatus sensitivity ($1 \cdot 10^{-3}$ 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. An inherent feature of the pulse-heating method is the fact that the values of p_c^m and T_c^m are always less than the true critical properties and should be corrected. The true critical constants of a stable compound are calculated by the following equations

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

Here $1/\pi_0$ and $1/\tau_0$ are correction factors.[2] The correction factors vary from $1/\pi_0 = 1.031$ and $1/\tau_0 = 1.003$ for methyl benzoate

---

* Corresponding author. E-mail: e-nikitin@mail.ru. Fax: +7-343-2678800.

10.1021/je700049s CCC: \$37.00

Table 2. Critical Temperatures and Pressures of *n*-Alkyl Benzoates: Experimental and Calculated Values

	T_c/K			p_c/MPa		
compound	exptl	ref 12	ref 13	exptl	ref 12	ref 13
methyl benzoate	695 ± 7^a 702 ± 1^b	684.1	676.6	3.46 ± 0.10^a 4.020 ± 0.200^b	3.568	3.589
ethyl benzoate	700 ± 7^a 707 ± 10^c	698.0	692.5	3.05 ± 0.09^a 3.480 ± 0.500^c	3.180	3.191
propyl benzoate	710 ± 7^a	710.9	707.5	2.60 ± 0.08^a	2.854	2.867
butyl benzoate	725 ± 7^a	723.0	721.5	2.40 ± 0.07^a	2.578	2.600
pentyl benzoate	736 ± 7^a	734.3	734.7	2.19 ± 0.07^a	2.342	2.378
hexyl benzoate	748 ± 7^a	745.0	747.2	1.98 ± 0.06^a	2.139	2.191
AAPE[d]		0.48	0.81		6.6	7.7
MAPE[e]		1.6	2.7		9.8	11

[a] This work. [b] Data from ref 1. [c] Estimated from the measurement of vapor pressure and two-phase heat capacity in ref 1. [d] AAPE = $(1/N)\left(\sum\left|Y_c^{\text{exptl}} - Y_c^{\text{calcd}}\right|/Y_c^{\text{exptl}}\right)\cdot 100$, where N is the number of experimental data points, $Y_c^{\text{exptl}}$is the experimental value of the critical property, and Y_c^{calcd} is the calculated value of the critical property. [e] MAPE = $\left(\left|Y_c^{\text{exptl}} - Y_c^{\text{calcd}}\right|_{\max}/Y_c^{\text{exptl}}\right)\cdot 100$.

to $1/\pi_0 = 1.044$ and $1/\tau_0 = 1.004$ for hexyl benzoate. The thermophysical properties required for calculating the correction factors are estimated by the principle of corresponding states using the formulas given in a previous paper.[5] The formulas contain a similarity parameter of the compound under investigation: the acentric factor or the analogous parameter suggested by Filippov[6]

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

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

The Filippov parameters and the critical constants of benzoates studied were calculated by an iteration method. For the first iteration, $p_c^m$and T_c^m were used as the critical constants, and the vapor pressure of methyl and propyl benzoates was calculated by the Antoine equation using parameters taken from the NIST Chemistry WebBook.[7] The vapor pressure of the rest of the benzoates was estimated by the following equation

$$\ln p_{\text{vp}} = B - \frac{C}{T} \qquad (2)$$

The parameters B and C were determined from the values of p_c^m and T_c^m and the normal boiling points. For ethyl, butyl, and pentyl benzoates, the normal boiling temperatures were taken from the NIST Chemistry WebBook,[7] and for hexyl benzoate, the normal boiling point was taken according to the Alfa Aesar recommendations.[8] 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. We restricted ourselves to two iterations because the correction factors showed little sensitivity to variations of the Filippov parameter.

In calculating the correction factors, two quantities are also needed: the ideal gas heat capacity of a substance under investigation and the factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation in a superheated liquid. The ideal gas heat capacity was estimated by the method of Rihani and Doraiswamy as presented by Reid et al.[9] The factor G_T was measured in one experiment with the critical constants as described previously[2] and estimated at 1.5 K^{-1}.

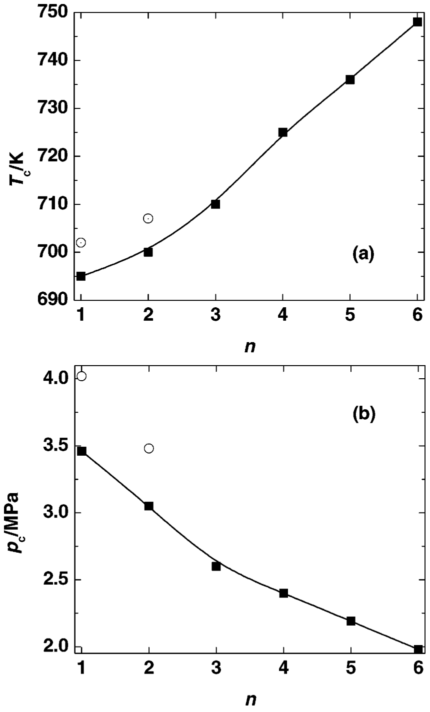

Figure 1. Critical temperatures (a) and pressures (b) of *n*-alkyl benzoates $C_6H_5COO(CH_2)_nH$ vs the number of CH_2 groups, *n*, in the alkyl radical: ■, this work; ○, ref 1.

The apparent critical constants of a thermally unstable compound measured 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 parameters of alkyl benzoates 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. From two to four samples of each compound were used. All the benzoates studied by us are unstable at their critical points.[1] However, in our experiments, the benzoates behaved as stable substances and no dependence of the apparent critical properties on the heating time t^* was detected; hence, the experimental data were averaged over all the probe lengths, heating times, and samples.

Uncertainties. The uncertainties of the critical constants measured by the pulse-heating method were discussed in detail in our previous papers.[10,11] As a rule, the pulse-heating method underestimates the critical temperature and pressure so that the results of measurements lie within the interval $Y - \delta_1$ to $Y + \delta_2$, where Y is the critical temperature or the critical pressure and $\delta_2 > \delta_1 > 0$. We have determined the value of δ_2 by comparing the values of the critical constants obtained by the pulse-heating technique and the literature data for several "standard" compounds (pentane, hexane, heptane, toluene, water, and naphthalene). For all of these substances, the pulse-heating method gives values lower than the literature ones. We cannot give a reliable estimation of δ_1 because the cases when the pulse-heating method overestimates the critical properties are sufficiently rare. In this situation, we are forced to give the uncertainties in the form $Y \pm \delta$, where $\delta = \delta_2$. We estimate the uncertainties for *n*-alkyl benzoates studied at 0.03 p_c and 0.01 T_c, where T_c is the absolute temperature. It corresponds to from (± 0.10 to ± 0.06) MPa for the critical pressure and to ±7 K for the critical temperature.

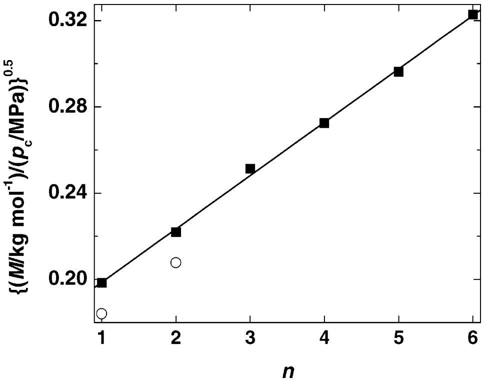

Figure 2. Correlation of the critical pressure of *n*-alkyl benzoates C_6H_5-$COO(CH_2)_nH$ as a function of the number of CH_2 groups, *n*, in the alkyl radical and molar mass: ■, this work; ○, ref 1.

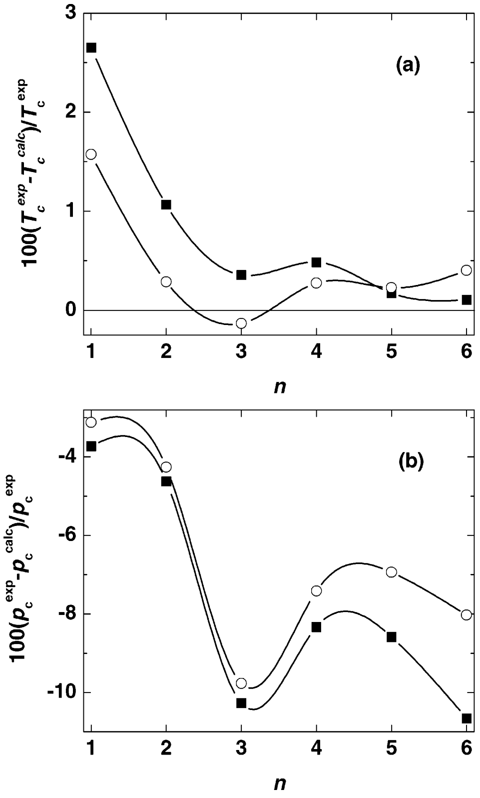

Figure 3. Percent deviations of the experimental critical temperatures (a) and pressures (b) of *n*-alkyl benzoates $C_6H_5COO(CH_2)_nH$ from the values calculated by group contribution methods as a function of the number of CH_2 groups, *n*, in the alkyl radical. GC methods: ○, ref 12; ■, ref 13.

Results and Discussion

The critical temperatures and pressures of *n*-alkyl benzoates included in this study are given in Table 2 and Figure 1. Previously, the critical temperature of methyl benzoate was derived by Steele et al.[1] from differential scanning calorimetry results. They also measured the vapor pressure at temperatures from (358.4 to 516.7) K and calculated the critical pressure by the Wagner equation. The critical temperature obtained by us is lower than that of Steele and co-workers, but the difference between them does not exceed the combined uncertainties. However, the critical pressures differ considerably. Partly, but not totally, it can be explained by the difference in the critical temperatures. If we calculate the critical pressure corresponding to the critical temperature measured by us using the vapor pressure equation suggested by Steele et al., we shall have $p_c = 3.695$ MPa, but Steele and co-workers obtained $p_c = 4.02$ MPa. The decomposition of ethyl benzoate precluded critical temperature measurements, and both the critical temperature and the critical pressure of this compound were determined by Steele et al. using a simultaneous least-squares fit of the vapor pressures and the two-phase heat capacities. The critical constants of ethyl benzoate measured by us are lower than those derived by Steele et al., but they lie in the range of the combined uncertainties. The well-known correlation by Lydersen[9] predicts that the quantity $(M/p_c)^{1/2}$ is a linear function of the number of CH_2 groups in a molecule of alkyl benzoate. Figure 2 shows that the points corresponding to the critical pressures determined by us fall on a straight line with acceptable accuracy. As noted above, the pulse-heating method has a tendency to underestimate the critical pressure and the critical temperature, but possible underestimation does not exceed the uncertainty of the critical constants and cannot explain the difference between the data by us and Steele et al. Figure 2 demonstrates that, more likely, the critical pressures of methyl and ethyl benzoates determined by Steele and coauthors are somewhat overestimated owing to the use of long-distance extrapolation, for about 185 and 166 K, respectively.

The critical constants of *n*-alkyl benzoates were also calculated by the group contribution methods of Constantinou and Gani[12] and Marrero and Gani[13] (Table 2). Percent deviations of the experimental critical constants from the values estimated by these methods are shown in Figure 3. Both of the methods give the critical temperatures of *n*-alkyl benzoates which are only slightly lower than the experimental values (except for propyl benzoate for the method of ref 11) so that the average absolute percent errors (AAPE) do not exceed the uncertainties of the experimental data. Both of the methods predict the critical pressures that are higher than the experimental values, and AAPE is more than twice the uncertainty of the experimental critical pressures.

Conclusion

The reliable critical temperatures and pressures of *n*-alkyl benzoates from methyl benzoate to *n*-hexyl benzoate have been measured using the pulse-heating technique. These data are useful for estimating the precision of the current predictive methods and developing new correlations for calculating the critical temperature and pressure.

Literature Cited

(1) Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Knipmeyer, S. E.; Nguyen, A. Thermodynamic properties and ideal-gas enthalpies of formation for methyl benzoate, ethyl benzoate, (*R*)-(+)-limonene, *tert*-amyl methyl ether, *trans*-crotonaldehyde, and diethylene glycol. *J. Chem. Eng. Data* **2002**, *47*, 667−688.

(2) Nikitin, E. D.; Pavlov, P. A.; Skripov, P. V. Measurement of the critical properties of thermally unstable substances and mixtures by the pulse-heating method. *J. Chem. Thermodyn.* **1993**, *25*, 869−880.

(3) Nikitin, E. D.; Pavlov, P. A.; Popov, A. P. Critical temperatures and pressures of 1-alkanols with 13 to 22 carbon atoms. *Fluid Phase Equilib.* **1998**, *149*, 223−232.

(4) Nikitin, E. D.; Pavlov, P. A.; Skutin, M. G. Acoustic method of measuring critical properties of thermally unstable substances. *Fluid Phase Equilib.* **1999**, *161*, 119−134.

(5) Nikitin, E. D.; Pavlov, P. A.; Bessonova, N. V. Critical constants of *n*-alkanes with from 17 to 24 carbon atoms. *J. Chem. Thermodyn.* **1994**, *26*, 177−182.

(6) Filippov, L. P. *Podobie Svoistv Veshchestv (Similarity of Substance Properties*); Moscow University Press: Moscow, 1978.

(7) Brown, R. L.; Stein, S. E. Boiling Point Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards

and Technology: Gaithersburg, MD 20899, June 2005 (http://webbook.nist.gov).

(8) http://www.alfa-chemcat.com.

(9) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

(10) Nikitin, E. D.; Popov, A. P.; Yatluk, Y. G. Critical temperatures and pressures of 12 phthalates using the pulse-heating method. *J. Chem. Eng. Data* **2006**, *51*, 1326−1330.

(11) Nikitin, E. D.; Popov, A. P.; Bogatishcheva, N. S.; Yatluk, Y. G. Critical temperatures and pressures of straight-chain dicarboxylic acids (C_4 to C_{14}). *J. Chem. Eng. Data* **2004**, *49*, 1515−1520.

(12) Constantinou, L.; Gani, R. New group contribution method for estimating properties of pure compounds. *AIChE J.* **1994**, *40*, 1697−1710.

(13) Marrero, J.; Gani, R. Group-contribution based estimation of pure component properties. *Fluid Phase Equilib.* **2001**, *183−184*, 183−208.

Received for review January 31, 2007. Accepted April 2, 2007. This study was supported by the Russian Foundation for Basic Research under grant 07-08-00107a and the grant of the President of the Russian Federation, NSh-4429.2006.8.

JE700049S