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Critical Temperatures and Pressures of Straight-Chain Saturated Dicarboxylic Acids (C_4 to C_{14})†

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The critical temperatures and pressures of nine saturated straight-chain dicarboxylic acids $HOOC(CH_2)_nCOOH$ with $n = 2, 3, 4, 5, 6, 7, 8, 10$, and 12 have been measured. All of the acids investigated are thermally unstable at their critical points. The method of pulse heating of a wire probe immersed in the liquid under study has been used. Residence times are from (0.01 to 1) ms. The experimental critical properties of dicarboxylic acids have been compared with the values calculated by the group-contribution methods of Ambrose, Joback, and Reid, Constantinou and Gani, and Marrero and Gani.

Introduction

Saturated dicarboxylic acids with straight-chain molecules $HOOC(CH_2)_nCOOH$ are an important class of compounds. They are used for the manufacture of polyamide plastics, in the fields of powder coating, pharmaceutics, and perfumery, as corrosion inhibitors, lubricants, hot melt adhesives, and so on. Nevertheless, the critical properties of dicarboxylic acids have probably never been measured. This is presumably explained by the fact that dicarboxylic acids begin to decompose at temperatures that are much lower than their critical temperatures. For example, according to the data of Degussa AG[1] for dodecanedioic acid, the temperature of the onset of decomposition is about 500 K, whereas our measurements give for the critical temperature a value of about 860 K. In this paper, we present the results of our measurements of the critical temperatures and pressures of nine dicarboxylic acids with $n = 2$, 3, 4, 5, 6, 7, 8, 10, and 12. We used the pulse-heating method applicable to thermally unstable substances.

Experimental Section

Method. The method and apparatus used in this work have been described in detail in earlier publications,[2−4] and only brief details are given below. The method consists of the measurement of the pressure dependence of the temperature of the attainable superheat (spontaneous boiling-up) of a liquid. When the pressure in the liquid approaches the critical pressure, the temperature of the attainable superheat approaches the critical temperature.[5,6] In the pulse-heating method, the liquid under study fills a Teflon cup with thin walls; the pressure outside the cup is created by a press and measured by a dial gauge. A platinum wire probe, 2×10^{-3} cm in diameter and (1 to 3) cm in length, is placed in the liquid. The probe is heated by rectangular pulses of electric current. By the end of a pulse, the probe and the liquid near it are heated to the temperature of spontaneous boiling-up. 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, a probe temperature perturbation arises from an abrupt change in the conditions of heat transfer from the probe to the liquid. The probe temperature is determined from its resistance at this moment. The probe temperature perturbation may be both positive and negative. The pressure in the liquid increases until the negative temperature perturbation drops to the level of the apparatus sensitivity (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. Calculating the process of boiling-up of a liquid on the probe has shown that the amplitude of the negative temperature perturbation approaches zero at a certain pressure that is close to but smaller than the critical pressure.[2,7] Therefore, the values of p_c^m and T_c^m are also smaller than the critical pressure and the critical temperature.

The true critical pressure p_c and critical temperature T_c of a stable compound are calculated by the following equation:

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

where $1/\pi_0$ and $1/\tau_0$ are correction factors.[2] To calculate these correction factors, the thermophysical properties of the substance under study near the critical point are required. They are estimated using the principle of corresponding states. The appropriate equations were given in the previous paper.[8] They contain the similarity parameter of a substance suggested by Filippov that is analogous to the acentric factor:[9]

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

where p_s is the vapor pressure. The Filippov parameters and the critical constants of dicarboxylic acids 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 pressures of dicarboxylic acids with $n = 3$ to 8 were estimated by the Antoine equation,[10] with $n = 2$ and 10 by the Clapeyron equation and boiling points taken in accordance with refs 10 and 11. Then the values of π_0 and τ_0 were calculated, and with the use of eq 1, p_c and T_c were calculated. For the second iteration, the Filippov parameter and the critical constants were calculated using the values obtained after the first iteration. Two iterations were enough because the values of π_0 and τ_0 are not very sensitive to the variations of Filippov's parameter. We failed to find in the literature the vapor pressure of tetradecanedioic acid ($n = 12$). The Filippov parameter of this acid was calculated by the following equation:

$$\log_{10}A = a_0 + a_1 n^{2/3}$$

The form of this equation was suggested by us in previous papers.[12,13] The constants a_0 and a_1 were determined by processing the Filippov parameters for $n = 2$ to 8 and 10: $a_0 = -0.1324$, $a_1 = 0.1832$.

For the calculation of the correction factors, the following quantities are also needed: the ideal gas heat capacity of the substance under study and the factor G_T. The ideal gas heat capacity was estimated by the method of Rihani and Doraiswamy as presented by Reid et al.[14] The factor $G_T \equiv \partial \ln J/\partial T$, where J is the rate of bubble nucleation in a superheated liquid, was measured in one experiment with the critical constants and estimated at 1.5 K^{-1}. The procedure of measuring this factor was described in our previous paper.[2]

Extrapolation Procedure. The critical temperature T_c and the critical pressure p_c determined in the way described above may depend on the time from the beginning of a heating pulse to the moment of boiling-up t^* because of the reactions of association−dissociation and decomposition of a substance under investigation in the course of heating. Dicarboxylic acids are known to be mixtures of monomers and associates. The influence of the reactions of association−dissociation and decomposition on the apparent critical constants measured in experiments with quick heating was discussed in our previous paper.[15] Following ref 15, let us consider a system that at the moment $t = 0$ has the temperature T_0, and then the temperature rises by the law

$$T = T_0 + bt \tag{2}$$

The dependence of the apparent critical temperature T_{ca} on the residence time t^* can be written as follows:

$$T_{ca}(t^*) = T_c + f[x(T(t^*)) - x_e(T_c)] + g[x_p(t^*)] \tag{3}$$

Here T_c is the true critical temperature that corresponds to equilibrium in accordance with the association−dissociation reaction and the absence of thermal decomposition, x is the mole fraction of monomers at the moment t^*, x_e is the equilibrium mole fraction of monomers, x_p is the mole fraction of products of decomposition, and f and g are some functions $f(0) = g(0) = 0$. In ref 15, it was demonstrated that for alkanoic acids the reaction of association−dissociation was very fast and at the residence times characteristic of the methods used today the mole fraction of monomers did not differ from the equilibrium mole fraction: $x[T(t^*)] \approx x_e(T_c)$. We failed to find in the literature the relaxation time of the reaction of association−dissociation for dicarboxylic acids. For simplicity, we shall ignore the association−dissociation reaction for dicarboxylic acids and assume the reaction of decomposition to have the form A → B + C. The concentration of substance A, c_A, changes in the course of heating in accordance with the equation

$$\frac{dc_A}{dt} = -c_A^m B \exp\left(-\frac{E}{RT}\right) \tag{4}$$

Here m is the order of the reaction, and we shall further suppose that $m = 1$; B is the preexponential factor, E is the activation energy, and R is the universal gas constant. Equation 4 together with eq 2 has an analytical solution. Usually $E/RT_0 > E/RT \gg 1$ so that we can expand the integral exponent function in the solution into a series and restrict it with three terms; the solution will have the following form:

$$c_A[T(t)] = c_{A0} \exp\left\{-\frac{BR}{bE}\left[T^2\left(1 - 2\frac{RT}{E}\right) \times \exp\left(-\frac{E}{RT}\right) - T_0^2\left(1 - 2\frac{RT_0}{E}\right)\exp\left(-\frac{E}{RT_0}\right)\right]\right\} \tag{5}$$

where $c_{A0} = c_A(t = 0)$. The concentration of the products of decomposition $c_p = c_B + c_C$ is governed in the course of heating by the equation

$$\frac{dc_p}{dt} = 2c_A B \exp\left(-\frac{E}{RT}\right) \tag{6}$$

The mole fraction of the decomposition products is equal to

$$x_p = \frac{c_p}{c_p + c_A} \tag{7}$$

We shall assume that function g in eq 3 has a simple form:

$$g = -ax_p(t^*) \tag{8}$$

where $a > 0$ is a constant. If the kinetic parameters of the reaction of the decomposition B and E as well as the parameter a are known, then eqs 3 and 5−7 allow us to calculate the dependence of the apparent critical temperature on heating time t^*. In Figure 1, such dependence is shown for a hypothetical compound with the following parameters: $T_c = 840$ K, $B = 10^{13}$ s^{-1}, $E = 170$ kJ·mol $^{-1}$, $a = 158$ K, $c_{A0} = 9 \times 10^3$ mol·m^{-3}, and $T_0 = 379$ K. However, as a rule, parameters B, E, and a are unknown. The critical constants of dicarboxylic acids were measured with the help of probes (1, 2, and 3) cm in length at heating times t^* = (0.03, 0.06, 0.11, 0.21, 0.46, and 1.00) ms. Several portions (from 3 to 5) of each acid were used. The results of measuring the critical temperature for pentanedioic acid are given in Figure 1. Each point in this Figure is the result of averaging over all of the lengths and all of the portions. Because of the scattering of the experimental points, it was difficult to extract the dependence $T_{ca}(t^*)$ at heating times from (0.03 to 0.11) ms, so the critical temperatures of the acids were determined by averaging the apparent critical temperatures over this interval of the heating times.

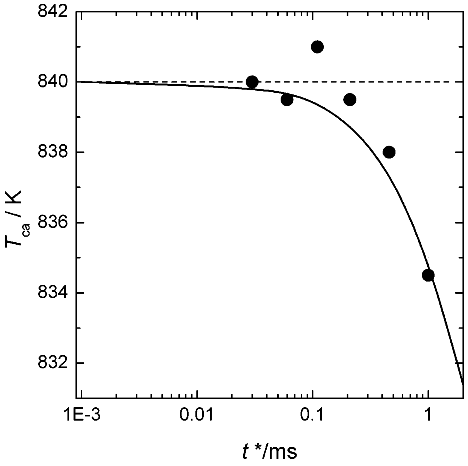

Figure 1. Apparent critical temperature of an unstable substance realized under a constant rate of heating as a function of the heating time. The solid line corresponds to the following parameters: E = 160 kJ·mol^{-1}, A = 10^{13} s^{-1}, c_{A0} = 9 × 10^3 mol·m^{-3}, a = 158 K, T_0 = 379 K. ●, Experimental values for pentanedioic acid. The dashed line corresponds to averaging the experimental values at heating times from (0.03 to 0.11) ms.

For the critical pressure, one can write an equation analogous to eq 3. However, we found no dependence of the apparent critical pressure on the heating time. The critical pressures of the acids were determined by averaging the experimental values of the critical pressures over all of the probe lengths and all of the heating times and portions.

Sources and Purities of the Compounds Studied. The sources and purities of the acids studied are given in Table 1. Before and after measuring the critical constants, the purities of the samples were determined using gas chromatography (Shimadzu GS-Ha) and proton magnetic spectroscopy (Bruker DRX 400). For the gas chromatography analysis, the dicarboxylic acids were transformed into their trimethylsilyl esters.[16] The sample of hexanedioic acid was found to contain cyclopentanone after measuring the critical properties. Butanedioic and pentanedioic acids are known to give the appropriate cyclic anhydrides under heating.[17] They were not detected by gas chromatography because in the course of trimethylsilylation the cyclic anhydrides gave the same products as the acids. However, proton magnetic spectroscopy showed the presence of the anhydrides in the samples that had undergone heating.

When measuring the critical constants by the pulse-heating method, it is important that the electrical conductivity of a substance under study is sufficiently low. Otherwise, the resistance and the temperature of the wire probe are measured improperly, and in addition, electrolysis of the substance on the probe takes place. The electrical conductivity of samples of dicarboxylic acids was measured by Dr. Sergey Shkerin from the Institute of High-Temperature Electrochemistry (Ekaterinburg) using the Impedance Measurement Unit IM-6 produced by Zahner electrik. The measurements were performed at frequencies of electric current from (2 to 8 × 10^5) Hz. No evident dependence of the electrical conductivity on frequency was revealed. The temperature of the sample was about 20 K higher than the melting temperature that corresponds to the conditions of measuring the critical constants. The electrical conductivity of the samples of dicarboxylic acids decreased from 9 × 10^{-3} Ω^{-1}·m^{-1} for butanedioic acid to 5 × 10^{-7} Ω^{-1}·m^{-1} for tetradecanedioic acid; estimations showed that for all of the acids studied electrical conductivity cannot interfere with measuring the critical properties.

Uncertainties. The uncertainties of the critical constants measured by the pulse-heating method were discussed in detail in our previous papers.[18,19] In most cases, but not always, the pulse-heating method underestimates the critical temperature and pressure. Strictly speaking, 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, δ_1 and δ_2 are the uncertainties, and $\delta_2 > \delta_1 > 0$. In a previous paper,[18] we explained in detail that the value of δ_2 was determined by comparing the literature values of the critical properties with those obtained by the pulse-heating method for some "standard" substances (pentane, hexane, heptane, toluene, water, and naphthalene). For all of the standard compounds, the pulse-heating method underestimates the critical properties. Now we cannot give a reliable estimation of δ_1 because the situation when the pulse-heating technique overestimates the critical constants is sufficiently rare, so we are forced to give the uncertainties in the form $Y \pm \delta$, where $\delta = \delta_2$. Dicarboxylic acids are associated substances, and the standard ones are not. This makes the uncertainties in calculating the correction factors $1/\pi_0$ and $1/\tau_0$ in eq 1 greater in the case of acids. We estimate the uncertainties for dicarboxylic acids at $0.04p_c$ and $0.015T_c$ except for butanedioic acid, the sample of which had a purity of only 95.7% after measuring the critical constants. For butanedioic acid, we give the following uncertainties: ±0.3 MPa and ±20 K.

Results and Discussion

The critical temperatures and pressures of dicarboxylic acids measured in this work are given in Tables 2 and 3. In these Tables, $\pm\delta T_c$ and $\pm\delta p_c$ are the uncertainties. Table 2 also lists the normal boiling temperatures of dicarboxylic acids. Experimental data for the boiling points of the acids are very limited. The normal boiling temperature of butanedioic acid was given in accordance with the data of Lancaster Synthesis;[11] it seems too low, but it was the only value we could find in the literature. For acids from pentanedioic to decanedioic, T_b was calculated by the Antoine equation with parameters recommended by NIST[10] and based on the Stull compilation of experimental data.[20] It is important that according to the NIST estimation the Antoine equation works up to atmospheric pressure for these acids. There are reduced-pressure boiling points for pentanedioic to dodecanedioic acids.[10,21] We estimated the normal boiling temperatures of these acids using these points, the Clapeyron equation, and the critical constants obtained by us. Table 2 shows that the estimation based on the reduced-pressure boiling points gives higher normal boiling temperatures than those calculated by the Antoine equation. Moreover, the lower the pressure at which the measurement has been performed, the higher the normal boiling temperature estimated. We considered the normal boiling temperatures calculated by the Antoine equation to be more reliable and used them further in the group-contribution methods. We failed to find in the literature any data for the vapor pressure of tetradecanedioic acid.

The dependence of the critical temperature on the number of CH$_2$ groups in a molecule (Figure 2) is characterized by two surprising features: (i) an unexpectedly high critical temperature of butanedioic acid and (ii) practically the same critical temperatures of the acids from pentanedioic to decanedioic. However, from Table 2 one can see that the dicarboxylic acids from hexanedioic to decanedioic have normal boiling temperatures that also depend weakly on the number of carbons, so the dependence of the quantity T_c/T_b on the number of CH$_2$ groups

Table 1. Sources and Purities of Acids Used in Critical Point Measurements

			purity/%				
			before measuring the critical constants			after measuring the critical constants	
acid	CASRN	supplier	supplier	gc	pms	gc	pms
butanedioic	110-15-6	Fluka	99.8	99.9	99.3	99.9	95.7
pentanedioic	110-94-1	Aldrich	99.20	99.9	99.7	99.8	99.0
hexanedioic	124-04-9	Riedel	100.2[a]	99.9	99.9	99.3	99.5
heptanedioic	111-16-0	Aldrich	99.90	99.9	99.9	99.9	99.9
octanedioic	505-48-6	Sigma	99.9	99.9	99.9	99.9	99.9
nonanedioic	123-99-9	Fluka	99.8	99.8	99.4	99.8	98.5
decanedioic	111-20-6	Aldrich	99.30	99.9	99.9	99.9	99.9
dodecanedioic	693-23-2	Aldrich	99.27	99.9	99.9	99.9	99.2
tetradecanedioic	821-38-5	Aldrich	99.10	99.4	99.4	99.4	99.4

[a] Calculated for the dried substance; water (Karl Fisher) ≤0.2%.

Table 2. Critical Temperatures of Dicarboxylic Acids $HOOC(CH_2)_nCOOH$: Experimental Values and Comparison with Predictive Methods (T_b Is the Normal Boiling Point)

				T_c/K			
n	T_b/K	T_c/K	$\pm\delta T_c$/K	ref 22	ref 23	ref 24	ref 25
2	508.2[a]	851	20	698.2	691.6	724.2	806.0
3	576.0[b] 602.7[c]	840	13	780.8	773.0	735.4	797.8
4	610.5[b] 617.9[c] 646.4[d]	841	13	817.4	808.7	746.0	807.4
5	615.1[b] 634.8[c]	842	13	814.4	805.1	756.0	816.6
6	618.6[b] 642.4[c,e]	843	13	810.4	801.0	765.5	825.5
7	630.2[b] 642.4[c] 650.0[e]	844	13	817.5	808.0	774.5	834.0
8	627.0[b] 650.9[c] 651.9[c]	845	13	806.0	796.9	783.1	842.2
10	675.8[c]	859	13	854.9	846.3	799.1	857.8
12		862	13			813.9	872.4
AAE[f]/K				45.69	54.30	81.03	20.90
AAPE[g]/%				5.40	6.42	9.57	2.47

[a] According to ref 11. [b] Calculated by the Antoine equation with parameters recommended by NIST.[10] [c] Calculated by the Clapeyron equation using the reduced-pressure boiling point.[10]. [d] Calculated by the Clapeyron equation using the reduced-pressure boiling point.[11] [e] Calculated by the Clapeyron equation using the reduced-pressure boiling point.[21] [f] $\mathrm{AAE} = (^1/_N)(\sum_{n=3}|T_c^{\mathrm{exptl}} - T_c^{\mathrm{calcd}}|)$. [g] $\mathrm{AAPE} = (^1/_N)(\sum_{n=3}|T_c^{\mathrm{exptl}} - T_c^{\mathrm{calcd}}|/T_c^{\mathrm{exptl}}) \times 100\%$, where N is the number of experimental data points, T_c^{exptl} is the experimental value of the critical temperature, and T_c^{calcd} is the calculated value of the critical temperature.

Table 3. Critical Pressures of Dicarboxylic Acids $HOOC(CH_2)_nCOOH$: Experimental Values and Comparison with Predictive Methods

			p_c/MPa			
n	p_c/MPa	$\pm\delta p_c$/MPa	ref 22	ref 23	ref 24	ref 25
2	6.59	0.30	4.130	4.932	4.936	4.710
3	4.27	0.20	3.595	4.328	4.304	4.020
4	3.85	0.15	3.182	3.829	3.790	3.536
5	3.28	0.13	2.854	3.412	3.364	3.148
6	2.97	0.12	2.587	3.059	3.010	2.832
7	2.72	0.11	2.365	2.759	2.710	2.571
8	2.50	0.10	2.178	2.500	2.455	2.354
10	2.15	0.09	1.881	2.081	2.047	2.014
12	1.90	0.08	1.655	1.760	1.738	1.764
AAE[a]/MPa			0.418	0.0685	0.0673	0.175
AAPE[b]/%			13.8	2.62	2.72	5.94

[a] $\mathrm{AAE} = (^1/_N)(\sum_{n=3}|p_c^{\mathrm{exptl}} - p_c^{\mathrm{calcd}}|)$. [b] $\mathrm{AAPE} = (^1/_N)(\sum_{n=3}|p_c^{\mathrm{exptl}} - p_c^{\mathrm{calcd}}|/p_c^{\mathrm{exptl}}) \times 100\%$, where N is the number of experimental data points, p_c^{exptl} is the experimental value of the critical pressure, and p_c^{calcd} is the calculated value of the critical pressure; in calculating AAE and AAPE, butanedioic acid is not taken into account.

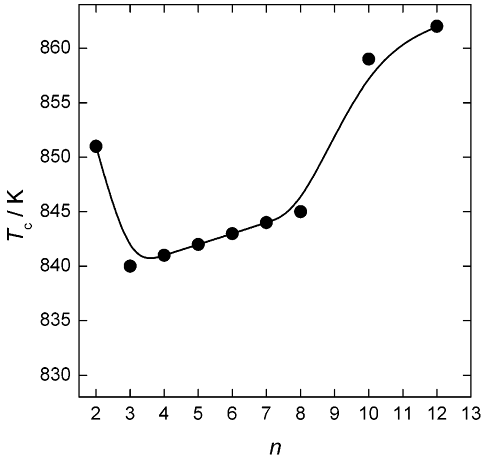

Figure 2. Critical temperatures of dicarboxylic acids $HOOC(CH_2)_nCOOH$ vs the number of CH_2 groups between the acid groups.

has a common form (Figure 3). The critical pressures of dicarboxylic acid are shown in Figure 4. They were also correlated with the number of CH_2 groups n and the molar mass M ($3 \leq n \leq 12$):

$$\left(\frac{M/\mathrm{kg\ mol^{-1}}}{p_c/\mathrm{MPa}}\right)^{1/2} = 0.11158 + 0.02154n \tag{9}$$

The result of the correlation is shown in Figure 5. When obtaining eq 9, we do not take into account butanedioic acid because the point representing this acid apparently drops out of the line. Thus, the critical temperature and pressure of butanedioic acid seem to be higher than may be expected. Butanedioic acid is known to decompose at temperatures above 570 K, giving butanedioic anhydride (2,5-dihydrofurandione) and water.[17] The critical properties of water are as follows:[10] $T_c = 647$ K, $p_c = 22.064$ MPa. The critical constants of butanedioic anhydride are unknown. The estimation by the method of Joback and Reid[23] gives the following values: $T_c = 809.3$ K, $p_c = 5.67$ MPa. Our samples of butanedioic acid after measuring the critical constants contained according to proton magnetic spectroscopy about 4% of these compounds. It is difficult to say if this amount could shift the critical point of butanedioic acid so noticeably. We must bear in mind that in the course of measuring, the amount of impurities increased; however, we

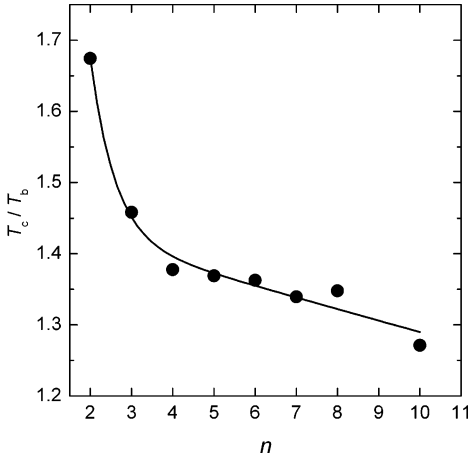

Figure 3. Correlation of the critical temperature of dicarboxylic acids HOOC$(CH_2)_n$COOH as a function of the number of CH_2 groups between the acid groups and the normal boiling point.

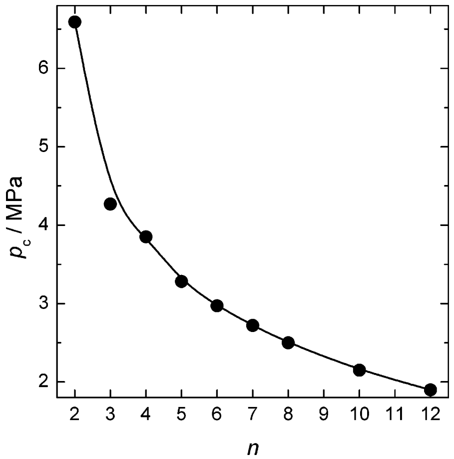

Figure 4. Critical pressures of dicarboxylic acids HOOC$(CH_2)_n$COOH vs the number of CH_2 groups between the acid groups.

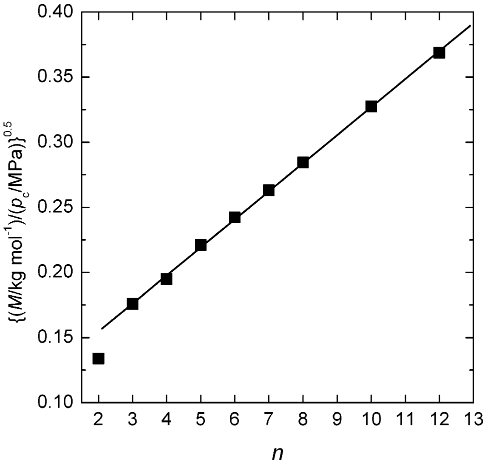

Figure 5. Correlation of the critical pressure of dicarboxylic acids HOOC$(CH_2)_n$COOH as a function of the number of CH_2 groups between the acid groups and molar mass.

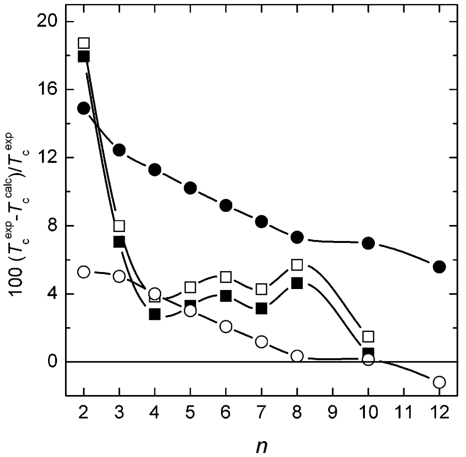

Figure 6. Percent deviations of the experimental critical temperatures from the values calculated by various group-contribution methods as a function of the number of CH_2 groups in dicarboxylic acids HOOC$(CH_2)_n$COOH. GC methods: ■, Ambrose;[22] □, Joback and Reid;[23] ●, Constantinou and Gani;[24] ○, Marrero and Gani.[25]

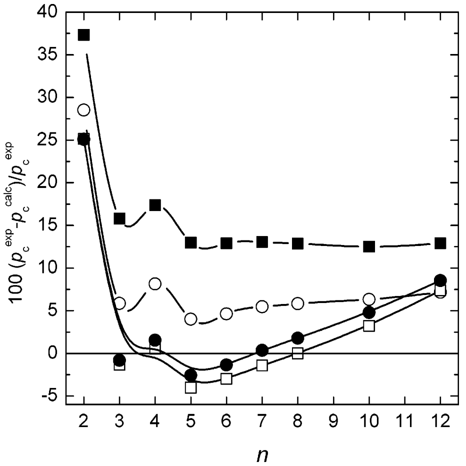

Figure 7. Percent deviations of the experimental critical pressures from the values calculated by various group-contribution methods as a function of the number of CH_2 groups in dicarboxylic acids HOOC$(CH_2)_n$COOH. GC methods: ■, Ambrose;[22] □, Joback and Reid;[23] ●, Constantinou and Gani;[24] ○, Marrero and Gani.[25]

detected no drift of the critical temperature or pressure of butanedioic acid.

Tables 2 and 3 contain the critical temperatures and pressures calculated by the well-known group-contribution methods of Ambrose as presented by Klincewicz and Reid,[22] Joback and Reid,[23] Constantinou and Gani,[24] and Marrero and Gani.[25] The percent deviations of the values calculated by these methods from the experimental values are shown in Figures 6 and 7. When estimating the critical temperatures calculated using the methods by Ambrose and Joback and Reid, one should bear in mind that these methods require the normal boiling temperatures, but modern measurements of them are absent. The method of Constantinou and Gani considerably underestimates the critical temperatures of dicarboxylic acids. This method is well known to use both contributions from the first- and the second-order groups. However, for dicarboxylic acids the authors give no second-order groups. This is probably the reason for the low accuracy in estimating the critical temperatures of dicarboxylic acids. The method of Marrero and Gani predicts the critical temperatures of dicarboxylic acids much better. The method uses the groups of the first, second, and third order. It is interesting that the Marrero and Gani method gives the local minimum in the critical temperature for pentanedioic acid in agreement with our measurements (Table 2). The best estimation of the critical pressure is provided by the methods of Joback and Reid and Constantinou and Gani. It is strange, but using the third-order groups in the Marrero and Gani method makes the prediction of the critical pressure worse in comparison with that of the Constantinou and Gani method. When calculating the values of AAE and AAPE for the critical temperatures (Table 2), we used the data for all of the acids. However, for the critical pressures (Table 3) we did not take into account butanedioic acid because the point representing this acid dropped out of the straight line in Figure 5.

Conclusions

The critical temperatures and pressures of nine saturated straight-chain dicarboxylic acids have been measured by the pulse-heating technique. The critical pressures of dicarboxylic acids have been correlated with the number of CH_2 groups between the acid groups in a molecule of the acid and the molar mass. We recommend this equation for the prudent extrapolation of the critical pressures.

Acknowledgment

We are grateful to Professor Kenneth Marsh for TRC boiling-point data of the acids and Dr. Sergey Shkerin (Institute of High-Temperature Electrochemistry, Ekaterinburg) for the measurements of the electrical conductivity of the acids.

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