J. Chem. Eng. Data **1997,** *42,* 278−280

Critical Properties of Alkanoic Acids Using the Sealed Ampule Method

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The critical temperatures and densities of the alkanoic acids containing up to ten carbon atoms have been measured using a sealed ampule method. Our critical temperature data show some disagreement with the data in the literature, due partly to differences in the experimental techniques used and partly to differences in the extrapolation techniques employed to determine the true critical properties of the substances. No published data on critical densities of the alkanoic acids were available for comparison. The performance of several group contribution methods has also been examined and shown to be poor for the critical properties of the homologous series of alkanoic acids.

Introduction

Alkanoic acids constitute one of the largest and most important groups of organic acids. They yield several derivatives such as esters, acid halides, anhydrides, and nitrites and consequently play an important role in various organic syntheses including the manufacture of plastics, elastomers, and other synthetic materials (Considine, 1974). As part of a continuing effort in the area of critical property measurement in our laboratory, we report below our measurements of the critical temperatures and densities of seven alkanoic acids using a sealed ampule method (Smith et al., 1986, 1987).

Experimental Section

A brief outline of the sealed ampule method is given below. Additional details are available in several publications (Smith et al., 1987; Teja et al., 1989; Anselme et al., 1990). In this method, a glass ampule is loaded with an amount of degassed liquid corresponding approximately to the amount that would yield the critical density of the pure substance when the ampule is sealed. The sealed ampule is then placed in a furnace where the fluid is alternately heated and cooled through its vapor−liquid transition temperature. The temperature and position of the meniscus disappearances and reappearances (when accompanied by critical opalescence) are recorded as a function of time using a real time data acquisition system. The actual critical temperature and critical density of the fluid are then obtained by extrapolation of the data. If the substance is thermally stable, the actual critical temperature and density are obtained by averaging the temperatures and densities of the disappearances and reappearances of the meniscus. However, for the alkanoic acids, the temperature of the meniscus disappearances and reappearances were found to decrease with time because of thermal decomposition of the substances. For these unstable substances, therefore, an extrapolation technique with a stability test was used to determine the true critical temperature and density.

Error in Critical Property Measurements

The determination of uncertainties in the experimental measurements is described in the following paragraphs.

The uncertainty in the critical temperature takes into account (i) differences in the loading and critical density, (ii) errors in calibration of thermocouples, (iii) errors in reading the multimeter voltage during the experiment, and (iv) lag time in temperature reading. In addition, 95% confidence intervals were chosen to fit the calibration data of the thermocouples. All sources amounted to an uncertainty in the critical temperature determination of $\Delta T_c = \pm 0.28$ K for a substance that is thermally stable. A more conservative uncertainty of $\Delta T_c = \pm 0.3$ K is therefore assumed to be the best attainable.

The critical density was obtained by linear interpolation of several experimental measurements of the disappearance and reappearance of the meniscus above or below the half volume position in the ampule. The factors which contribute to the uncertainties in the critical density measurement are (i) calibration of the ampules with acetone, (ii) errors in the volume caused by sealing the ampule (iii) errors in loading the substance during the experiment, and (iv) errors in determining the meniscus position during the experiment. Evaluation of these errors led to an estimate for the experimental uncertainty in the critical density of $\Delta\rho_c = \pm 0.0045$ g/cm^3. A more conservative value of $\Delta\rho_c = \pm 0.005$ g/cm^3 was therefore adopted in this work. About 90% of this error is associated with the measurement of the position of the meniscus disappearance/reappearance in the ampule.

For thermally unstable substances, such as the alkanoic acids, an extrapolation technique and a stability test were used to determine the true critical temperature and density of the substance and their uncertainties. The extrapolation technique is based on the following assumptions: (i) the critical locus of the mixture of the original substance and its products of reaction is a linear function of the mole fraction of the reaction products, and (ii) the reaction rate increases with temperature. Extrapolation to the “true” critical temperature of the undecomposed substance is carried out as follows. An average value of the first disappearance and reappearance temperature is calculated. The same is done with the second disappearance and reappearance. Both values are assigned to their respective average times. This averaging process minimizes bias in the data due to lag time on the temperature measurement. The two data points generated are then linearly extrapolated to a time when no decomposition is known to have occurred (see below), which gives a “high” estimate of the critical point. The average of the first disappearance/reappearance gives the lowest possible value for the critical temperature. The midpoint between the upper and lower estimates is taken as the “true” critical point. The error

S0021-9568(96)00231-2 CCC: $14.00

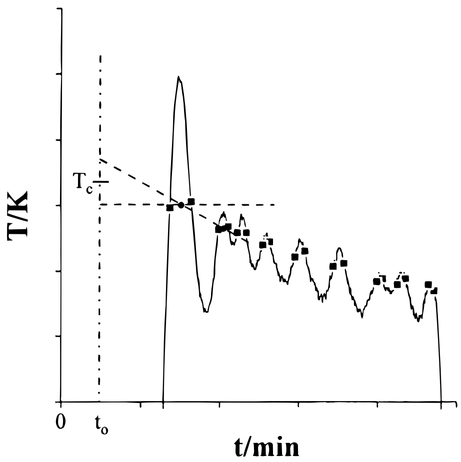

Figure 1. Extrapolation of meniscus disappearance/reappearance data. Note that the substance was determined to be undecomposed at a temperature on the temperature−time trace which corresponded to time t_0 on the trace.

Table 1. Sources and Purities of the Materials

substance	purity	source
propanoic acid	>99.5%	Fluka
butanoic acid	>99.5%	Fluka
pentanoic acid	>99%	Fluka
hexanoic acid	>99%	Sigma
heptanoic acid	>99%	Fluka
octanoic acid	>99%	Sigma
decanoic acid	>99%	Sigma

margin was assumed to be half the interval between the upper and lower points. This extrapolation method is illustrated in Figure 1.

To shorten the temperature extrapolation interval for thermally decomposing substances, a stability test was carried out. A loaded ampule was subjected to the same heating profile but heated to a temperature below the critical temperature of the substance. This test temperature was maintained constant within 1 to 2 K for a period of time that corresponded to the time that was required to heat the substance to that temperature in the actual experimental run. The ampule was then quenched to room temperature, and its contents were analyzed. A gas chromatograph, with a Gaschrom 254 column, and a thermal conductivity detector were used in the analysis. The chromatogram was compared with that of the pure substance, and if no difference could be detected, the substance was considered to be stable at the test temperature. From several of these tests, the highest temperature of stability could be determined, leading to a time when the substance is still undecomposed during the actual experimental run. The extrapolation of the critical temperature was then carried back to that time, as illustrated in Figure 1.

For propanoic, butanoic, and pentanoic acids studied in this work, the uncertainties determined from the extrapolation technique were lower than the best uncertainties determined for thermally stable substances (±0.3 K for temperature and ±0.005 g/cm^3 for density). Therefore the more conservative values of ±0.3 K and ±0.005 g/cm^3 were adopted for these substances. Uncertainties for hexanoic and higher acids were found to be significantly larger than those for the lower member of the homologous series.

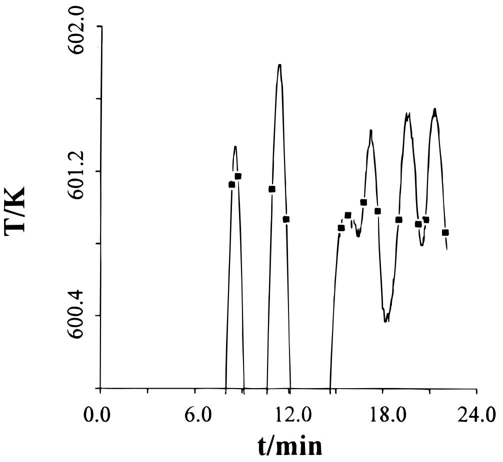

Figure 2. Experimental temperature−time trace for propanoic acid.

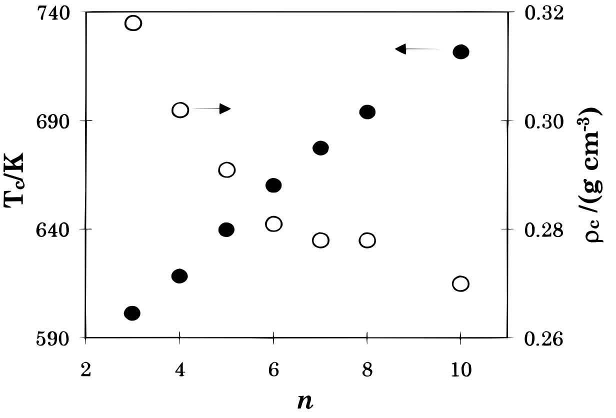

Figure 3. Critical temperatures and densities of the alkanoic acids as a function of carbon number.

Sources and Purities of the Substances Studied

The purest commercially available materials were used in the experiments. The sources and purities are given in Table 1. The purities were checked by gas chromatography and found to be equal to or higher than the purities stated by the manufacturer. The substances were therefore used without further purification.

Results and Discussion

Figure 2 shows the experimental temperature−time trace for propanoic acid, with meniscus disappearances and reappearances shown by the data points. Propanoic acid was found to be mildly unstable at all temperatures (temperatures of meniscus appearances and disappearances changed slowly with time, as shown in Figure 1). Starting with hexanoic acid, the apparent critical temperature decreased significantly with time due to thermal decomposition of the substance.

Results for all seven alkanoic acids are summarized in Table 2, together with data from the literature. The values reported by Ambrose and Ghiassee (1987) for the critical temperatures of the alkanoic acids were generally higher than the values obtained in this work, although agreement was within the combined uncertainties of the two sets of measurements for heptanoic, octanoic, and decanoic acids. The discrepancies for the lower members of the series may be due to two factors. First, the thermocouple in Ambrose and Ghiassee's experiment was not intimately in contact with the fluid, unlike the thermocouple used in this work. This may have led to larger errors in their values due to lag time. Secondly, different extrapolation techniques were used in the two studies. Values given by Ambrose and Ghiassee (1987) were always the result of linear extrapolation to zero time, rather than to a time when the substance was known to be undecomposed. This would generally lead to critical temperatures that are too high.

Table 2. Experimental Results and Critical Data for the Critical Properties of Alkanoic Acids

substance	T_c/K	ρ_c/g cm^{-3}	ref
propanoic acid	601.3 ± 0.3	0.318 ± 0.005	this work
	604 ± 0.5		Ambrose and Ghiassee (1987)
	613.05 ± 6.0		Brown (1906)
	602.15 ± 2.0		Efremova and Sokolova (1972)
	612		Vespigniani (1903)
butanoic acid	618.3 ± 0.3	0.302 ± 0.005	this work
	624 ± 1		Ambrose and Ghiassee (1987)
	627.9 ± 6.0		Brown (1906)
pentanoic acid	639.7 ± 0.3	0.291 ± 0.005	this work
	639.9 ± 0.4	0.300 ± 0.006	Teja and Anselme (1990)
	643 ± 2		Ambrose and Ghiassee (1987)
	652.02 ± 6.0		Brown (1906)
hexanoic acid	660.2 ± 0.6	0.281 ± 0.005	this work
	663 ± 1		Ambrose and Ghiassee (1987)
heptanoic acid	677.3 ± 0.7	0.278 ± 0.005	this work
	679 ± 1		Ambrose and Ghiassee (1987)
octanoic acid	694.0 ± 1.0	0.278 ± 0.005	this work
	694 ± 1.5		Ambrose and Ghiassee (1987)
decanoic acid	721.6 ± 3.5	0.270 ± 0.005	this work
	726 ± 4		Ambrose and Ghiassee (1987)

Table 3. Comparison of Estimation Techniques

method	ΔT_c/K	Δv_c/cm^3 mol^{-1}
Ambrose	7.78	12.9
Joback	7.16	12.8
Fedors	10.3	
Somayajulu	6.48	18.6

The correlation between the critical properties of alkanoic acids and carbon number is shown in Figure 3. We have also compared some of the commonly used group contribution methods for their ability to predict the critical properties of the alkanoic acids. The methods included those of Ambrose (1978), Joback (1984), Somayajulu (1989), and Fedors (1979). The results are summarized in Table 3. In general, all the methods overestimate the critical temperature and underestimate the critical volume of the alkanoic acids. An average absolute error of at least 6 K was obtained for the critical temperature and 12 cm^3/mol for the critical volume.

Conclusions

The critical temperatures and densities of seven alkanoic acids have been measured using the sealed ampule method. Our data show some disagreement with the data published previously by Ambrose and Ghiassee (1987), which can be attributed partly to differences in the experimental techniques used and partly to differences in the extrapolation techniques employed to determine the true critical properties of the substances. We have also compared several group contribution methods for their ability to predict the critical properties of the alkanoic acids and found that all the methods yield unsatisfactory results for the critical properties of the homologous series of alkanoic acids.

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Received for review July 9, 1996. Accepted November 18, 1996.⊗

JE960231E

⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.