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Critical Temperatures and Densities of *n*-Alkanones

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Critical temperatures and densities of 24 *n*-alkanones with 10–14 carbon atoms have been measured. These alkanones were found to be thermally unstable at temperatures below their critical temperature, whereas in an earlier publication, it was reported that alkanones with fewer than 10 carbon atoms were thermally stable up to their critical temperatures. The data show smooth behavior of the critical temperatures and densities with carbon number for these substances. The critical temperatures of the isomeric *n*-alkanones increase with increasing carbon number, but the critical densities decrease as the carbon number increases. Both properties approach those of the corresponding *n*-alkane as the carbon number increases. In addition, the critical temperatures of the *n*-alkanones decrease as the carbonyl group is located further toward the center of the carbon chain, while the critical densities remain virtually constant. New correlations are reported for the critical temperature and density of members of the *n*-alkanone series.

Critical properties are important characterization parameters for pure substances. However, the existing database of these properties for pure substances is small and mainly confined to stable substances. Data for thermally unstable substances are generally scarce and sometimes of questionable accuracy.

In this work, the critical temperatures and densities of *n*-alkanones with 10–14 carbon atoms have been measured. The behavior of the critical temperatures and densities with carbon number for these substances has also been studied, as has the effect of the position of the carbonyl group on critical properties. New correlations are reported for the critical temperature and density for the homologous series of *n*-alkanones using the data reported in the present work as well as data for *n*-alkanones with fewer than ten carbon atoms from our earlier work (Pulliam et al., 1994).

Experimental Section

A sealed ampule method was used in this work for the measurement of the critical properties. The method and apparatus have been described in detail in earlier publications (Teja et al., 1989; Anselme et al., 1990; Anselme and Teja, 1990a–c; Gude and Teja, 1994), and only an outline is given below. Glass ampules, of known volume, were loaded with an amount of substance corresponding to the amount required to yield the estimated critical density. Each ampule was then mounted in a holder inside a stainless steel block. The block offered protection against explosions and was equipped with two quartz windows 180° apart for visual observation of the contents of the ampule. A hot nitrogen gas stream was used to heat the sample until the critical point was attained. After the first observation of the critical point, noted by meniscus disappearance and the occurrence of critical opalescence, the substance was alternately cooled and heated through the critical region. The temperature–time behavior of the substance during successive meniscus disappearances and reappearances was recorded on a real time data acquisition system. Also, a magnified image of the ampule was recorded on a video recorder, and a video/computer image overlaying device allowed the actual temperature of the sample and the time from the beginning of the experiment to be displayed in real time on the video screen. This magnified image of the ampule containing the sample allowed the critical density to be measured by locating the meniscus disappearance with respect to the half-volume mark of the ampule. The half-volume of the ampule was determined and marked during calibration of the ampule and denotes the position where the vapor and liquid phases in equilibrium occupy the same volume. At least three runs were made for each substance so that deviations of the meniscus disappearance with respect to the half-volume mark could be interpolated to a value indicating the critical density of the substance.

After the critical behavior had been established, each substance was studied in a second apparatus that employed a platinum heater as described by Gude and Teja (1994). Although the platinum heater is more sluggish in its temperature response than the gas heater, it provided better temperature control. As before, the critical temperatures and densities of each substance were measured by alternately heating and cooling a sealed glass ampule containing a sample of the substance, while the temperature–time behavior and the position of the meniscus were recorded on a real time data acquisition system. Furthermore, the recorded data were analyzed to obtain values of the critical temperature and density. A typical trace of the temperature–time behavior for 3-tetradecanone using this apparatus is shown in Figure 1. The meniscus reappearances/disappearances are shown by the solid squares and exhibit a steady decrease with time, which indicates that 3-tetradecanone is thermally unstable in the critical region. Also, the solid line represents the temperature–time trace from the beginning of the experiment at room temperature to the end of the experiment. The data were analyzed using the extrapolation technique of Gude and Teja (1994) to obtain the reported values of the critical temperature and density of each substance.

Sources and Purity

Table 1 gives the purity of the substances studied. All samples were purchased from Wiley Organics and were of the highest commercially available purity. They were used without further purification.

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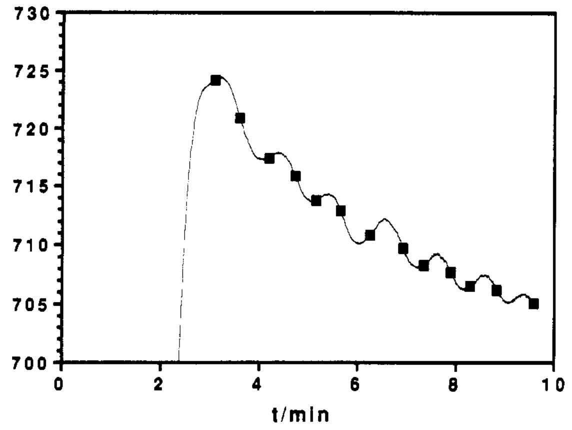

Figure 1. Temperature versus time behavior of 3-tetradecanone in the platinum furnace. The squares denote meniscus disappearances or reappearances.

Table 1. Purity of Substances Studied

substance	purity/mol %	substance	purity/mol %
2-decanone	>99	5-dodecanone	>99.5
3-decanone	>99.5	6-dodecanone	>99.5
4-decanone	>99.5	2-tridecanone	>97
5-decanone	>99	3-tridecanone	>97
2-undecanone	>99	4-tridecanone	>98
3-undecanone	>99.5	5-tridecanone	>99
4-undecanone	>99.5	6-tridecanone	>98
5-undecanone	>99	7-tridecanone	>99
6-undecanone	>99.5	2-tetradecanone	>98
2-dodecanone	>99	3-tetradecanone	>99.5
3-dodecanone	>98	4-tetradecanone	>97
4-dodecanone	>99.5	7-tetradecanone	>98

Table 2. Literature Values of the Critical Temperatures and Densities of Alkanones with Two to Nine Carbon Atoms

1-alkanone	T_c/K	ρ_c/g·cm^{-3}
2-propanone	508.1[a]	0.278[a]
2-butanone	536.8[a]	0.270[a]
2-pentanone	561.1[a]	0.286[a]
3-pentanone	560.6[a]	0.256[a]
2-hexanone	586.6 ± 0.4[b]	0.267 ± 0.003[b]
3-hexanone	583.2 ± 0.2[b]	0.265 ± 0.003[b]
2-heptanone	611.4 ± 0.3[b]	0.262 ± 0.003[b]
3-heptanone	606.6 ± 0.2[b]	0.264 ± 0.003[b]
4-heptanone	602.0 ± 0.2[b]	0.263 ± 0.003[b]
2-octanone	632.7 ± 0.2[b]	0.258 ± 0.003[b]
3-octanone	627.7 ± 0.2[b]	0.258 ± 0.003[b]
4-octanone	623.8 ± 0.2[b]	0.258 ± 0.003[b]
2-nonanone	652.5 ± 0.2[b]	0.254 ± 0.003[b]
3-nonanone	648.1 ± 0.2[b]	0.254 ± 0.003[b]
4-nonanone	643.7 ± 0.3[b]	0.254 ± 0.003[b]
5-nonanone	641.4 ± 0.3[b]	0.254 ± 0.003[b]

[a] Ambrose and Ghiassee (1987). [b] Pulliam et al. (1994).

Results and Discussion

The critical temperatures and densities of 24 alkanones from decanone to tetradecanone were measured. The experimental results after analysis are presented in Tables 2 and 3. Also shown are our results for the *n*-alkanones with fewer than 10 carbon atoms reported in an earlier publication (Pulliam et al., 1994) and available literature data for the lower members of the series (Ambrose and Ghiassee, 1987). All temperatures are expressed according to ITS-90. For thermally stable substances, our measured critical temperatures are reproducible within ±0.08 K, with a maximum error from all sources estimated to be ±0.3 K. Thus, our value for the uncertainty in temperature measurements for stable substances is $\Delta T_{\mathrm{exp}} = \pm 0.3$ K. For thermally unstable substances, additional errors due to extrapolation lead to an uncertainty in temperature measurement in the range $\Delta T_{\mathrm{exp}} = \pm 0.5-4.8$ K. The error from all sources in density measurements of thermally stable substances is estimated to be ±0.003 g·cm^{-3}, while that for unstable substances is estimated to be ±0.007 g·cm^{-3}.

Table 3. Critical Temperatures and Densities of Alkanones with 10–14 Carbon Atoms Measured in this Work

n-alkanone	T_c/K	ρ_c/g·cm^{-3} ± 0.007
2-decanone	671.8 ± 0.5	0.250
3-decanone	667.6 ± 0.5	0.249
4-decanone	662.9 ± 0.5	0.249
5-decanone	661.0 ± 0.4	0.249
2-undecanone	687.8 ± 1.6	0.246
3-undecanone	684.6 ± 1.3	0.246
4-undecanone	680.9 ± 1.6	0.246
5-undecanone	679.4 ± 1.5	0.246
6-undecanone	678.5 ± 1.5	0.246
2-dodecanone	702.1 ± 2.7	0.245
3-dodecanone	700.7 ± 1.4	0.245
4-dodecanone	696.6 ± 1.5	0.243
5-dodecanone	695.2 ± 3.0	0.243
6-dodecanone	694.2 ± 1.2	0.242
2-tridecanone	717.0 ± 3.3	0.242
3-tridecanone	716.1 ± 2.7	0.241
4-tridecanone	711.6 ± 3.5	0.241
5-tridecanone	709.7 ± 4.5	0.240
6-tridecanone	709.3 ± 2.7	0.240
7-tridecanone	708.2 ± 2.8	0.239
2-tetradecanone	727.7 ± 4.8	0.237
3-tetradecanone	726.8 ± 3.7	0.237
4-tetradecanone	725.2 ± 3.7	0.236
7-tetradecanone	722.9 ± 4.2	0.235

In our previous work (Pulliam et al., 1994), the *n*-alkanones from the *n*-hexanones to the *n*-nonanones were found to be thermally stable, since their critical temperatures remained constant with time in the critical region. However, a noticeable decrease in apparent critical temperature during an experiment was observed for the *n*-decanones, for which the temperature decreased by 1.0 K in about 10 min. A change in location of the meniscus disappearance/reappearance was also noticed. This change was marked for the very thermally unstable *n*-tridecanones and *n*-tetradecanones. Furthermore, as the concentration of the reaction byproducts increased, the otherwise narrow temperature region of critical opalescence broadened.

The results show that the critical temperatures of the alkanones increase with increasing carbon number, as expected. As is the case with homologous series of *n*-alkyl substances, the critical temperatures of the alkanones approach those of the *n*-alkane series as the carbon number increases (Figure 2). Furthermore, the critical temperatures of the isomeric alkanones of equal carbon number decrease as the carbonyl group moves further into the center of the carbon chain (Figure 3). This effect diminishes as the carbon chain increases (Figure 3). Similarly, as the carbonyl group was located further toward the center of the alkanone carbon chain, the decomposition rate also decreased.

The effect of the carbonyl group was noticeable when the critical temperatures of the lower members of the *n*-alkanone series were compared to those of the *n*-alkanal series. The lower *n*-alkanones (acetone to 5-nonanone) were found to be stable at all temperatures, whereas Gude and Teja observed that the alkanals (*n*-propanal to *n*-decanal) were highly unstable at temperatures below their critical temperatures. The unstable behavior of the *n*-alkanals can be attributed to aldol addition and decomposition at elevated temperatures. Alkanals with six or fewer carbon atoms undergo aldol addition in which the formation of dimers causes the critical temperature to increase

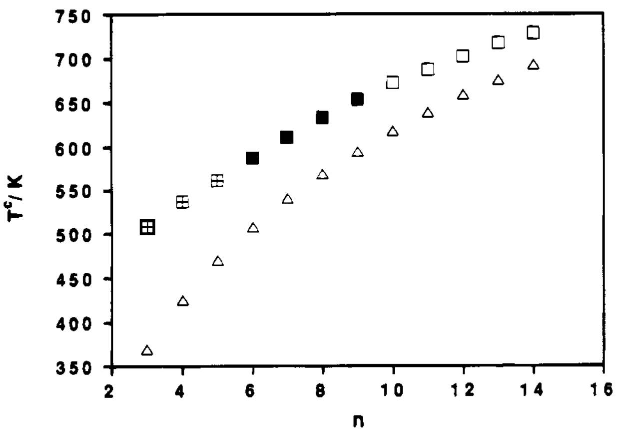

Figure 2. Critical temperatures of the 2-alkanones and *n*-alkanes as a function of carbon number: (△) *n*-alkanes (Tsonopoulos and Tan, 1993); (square with cross) 2-alkanones (Ambrose and Ghiassee, 1987); (■) 2-alkanones (Pulliam et al., 1994); (□) 2-alkanones (this work).

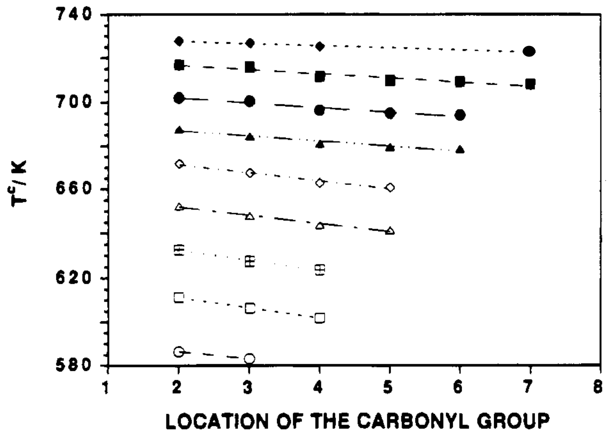

Figure 3. Difference in the critical temperatures of isomeric *n*-alkanones as a function of the carbonyl group location: (○) *n*-hexanone; (□) *n*-heptanone; (square with cross) *n*-octanone; (△) *n*-nonanone; (◇) *n*-decanone; (▲) *n*-undecanone; (●) *n*-dodecanone; (■) *n*-tridecanone; (◆) *n*-tetradecanone.

with time. This is due to the carbonyl group being located at the first carbon of the alkanal, in which a carbanion generated from one *n*-alkanal molecule adds to the carbonyl group of a second molecule to form a β-hydroxyaldehyde (Morrison and Boyd, 1973). The alkanones studied in the present work do not have an α-hydrogen available for the aldol addition reaction to proceed, and as a result dimerization cannot occur. Decomposition appears to be the dominant reaction occurring for higher members of both the *n*-alkanal and *n*-alkanone series, which leads to decreasing critical temperatures with residence time.

The critical densities of the alkanones decrease with increasing carbon number (Figure 4). Furthermore, the critical densities of isomers with equal carbon numbers remain virtually constant as the carbonyl group moves further into the center of the carbon chain. The location of the carbonyl group does not apparently change the molecular packing of the liquid; therefore, the critical density remains approximately constant. As is the case with the critical temperature, the critical densities of the alkanones approach the corresponding alkane values as the carbon number increases (Figure 5).

Several group contribution methods for the prediction of the critical temperatures and densities of the *n*-alkanones are compared in Table 4 (Fedors, 1973; Reid et al., 1986; Somayajulu, 1989). With the exception of the Fedors method, good agreement was obtained between prediction and experiment. The percent deviations from the experimental values were generally less than 1%, except for the Fedors method, for which the percent deviation was 11%. Although the methods work well for the 2-alkanones, they cannot distinguish between isomers because they do not contain a group contribution parameter for the location of the carbonyl group.

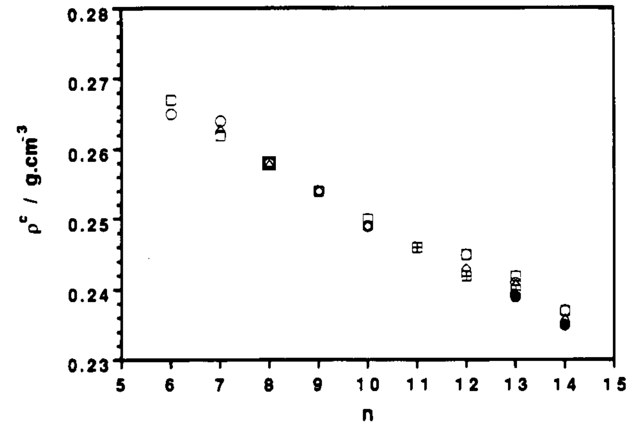

Figure 4. Critical densities of the isomeric alkanones as a function of carbon number. (□) 2-alkanones; (○) 3-alkanones; (△) 4-alkanones; (◇) 5-alkanones; (square with cross) 6-alkanones; (●) 7-alkanones. All values are from Pulliam et al. (1994) and this work.

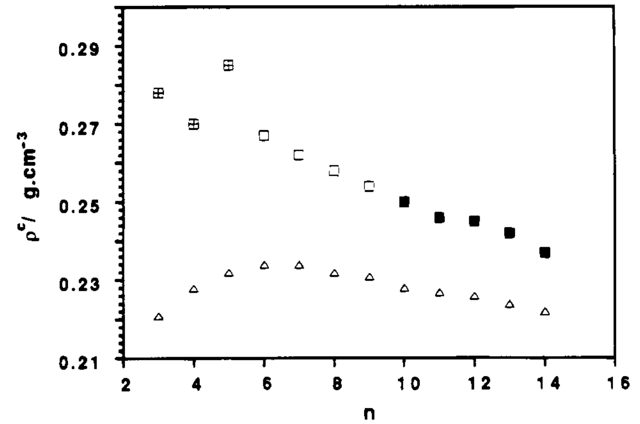

Figure 5. Critical densities of the 2-alkanones and *n*-alkanes as a function of carbon number: (△) *n*-alkanes (Tsonopoulos and Tan, 1993); (square with cross) 2-alkanones (Ambrose and Ghiassee, 1987); (□) 2-alkanones (Pulliam et al., 1994),; (■) 2-alkanones (this work).

Table 4. Comparison of Prediction Methods for *n*-Alkanones with the New Correlation in This Work

method	$\frac{1}{n}\sum \lvert T_{c,calcd} - T_{c,exptl}\rvert$	$\left(\frac{1}{n}\sum \left\lvert \varrho_{c,exptl} - \varrho_{c,calcd}\right\rvert\right) / \varrho_{c,exptl} \times 100$
Ambrose	4.80 K	4.11%
Joback	6.23 K	3.50%
Somayajulu	4.92 K	4.34%
Fedors	53.90 K	7.07%
this work	0.92 K	0.81%

The group contribution methods also failed to predict the critical densities of the alkanones (Figure 6). Furthermore, the difference in density between an alkanone and its corresponding *n*-alkane approaches zero as the carbon number increases, but the methods failed to predict this trend (Figure 6).

Correlation

Table 5 contains the results of a fit of the data using a relationship that has been applied successfully to the

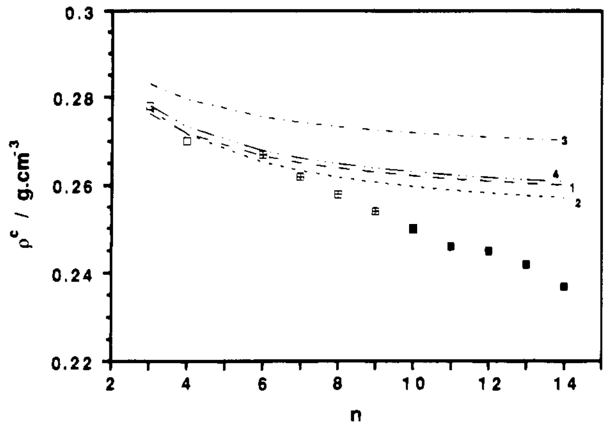

Figure 6. Comparison of prediction methods with experimental data: (□) 2-alkanones (Ambrose and Ghiassee, 1987); (square with cross) 2-alkanones (Pulliam et al., 1994); (■) 2-alkanones (this work); (line 1) Ambrose; (line 2) Joback; (line 3) Fedors; (line 4) Somayajulu.

Table 5. Constants of Equation 1

	T_c/K		ϱ_c/g·cm^{-3}	
	A_T	B_T	A_ϱ	B_ϱ
2-alkanones	570.8711	1.1363	0.2272	1.0469
3-alkanones	524.2179	0.8317		
4-alkanones	523.3036	1.5404		
5-alkanones	464.4444	0.7479		

critical properties of a number of homologous series (Gude and Teja, 1994; Teja et al., 1989, 1990). The general expression for any alkyl substance ($n_C \geq 3$) is :

$$X_c = X_{c,\text{alkane}} + \frac{A_x}{B_x + n_C} \tag{1}$$

where X_c is the critical property of the alkyl substance of interest, $X_{c,\text{alkane}}$ is the same property for the corresponding n-alkane, and n_C is the carbon number. A_x and B_x are constants for each homologous series property of interest (T_c or ϱ_c). The constants calculated for the critical temperatures and densities of alkanones with three or more carbon atoms are given in Table 5. Critical properties of the n-alkanes used in the correlation were obtained from Tsonopoulos and Tan (1993).

In Table 5, A_T and B_T depend on the location of the carbonyl group along the carbon chain, and therefore different values of the constants are reported for the critical temperatures of each isomeric series. The overall average percent deviation between experimental and calculated critical temperatures was 0.92 K. Since the isomeric alkanones showed little variation in the critical densities, only one set of constants is shown for this property. The deviations between correlation and experiment are shown in Table 4.

Conclusions

New measurements for the critical temperatures and densities of the n-alkanone series with 10–14 carbon atoms are reported. A total of 24 substances were investigated. The n-alkanones studied were found to be thermally unstable at temperatures below their critical temperature. Furthermore, our data show smooth behavior of the critical temperature and density with carbon number for the substances studied, with both properties approaching those of the corresponding n-alkane at large carbon numbers. The critical temperatures of the isomeric n-alkanones increase with increasing carbon number, whereas the critical densities decrease as the carbon number increases. In addition, the critical temperatures of the n-alkanones decrease as the carbonyl group is located further toward the center of the carbon chain, while the critical densities remain virtually constant. New correlations were also developed for the critical temperatures and densities of the n-alkanones.

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