Gas−Liquid Critical Temperatures of Some Alkenes, Amines, and Cyclic Hydrocarbons

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The gas−liquid critical temperatures of 23 alkenes (C_5−C_8), 8 amine compounds (C_3−C_8), and 8 cyclic hydrocarbons (C_8−C_{10}) are reported. These values, together with the previously reported critical temperatures for alkenes, amines, and cyclic hydrocarbons, provide extended data sets which can be used to develop more accurate correlations for predicting the critical temperatures of these alkene, amine, and cyclic hydrocarbon compounds. The majority of compounds whose critical temperatures are reported here have not been previously investigated.

Introduction

A knowledge of the gas−liquid critical properties of substances is important because these properties can be used to predict various thermodynamic parameters using the principle of corresponding states. Correlation equations are often used to expand the critical property data set for a group of substances.[1−5] Their accuracy is often restricted because of (i) the limited number of reliable gas−liquid critical property measurements and (ii) their poor predictive power. In addition, the reliability of some of the earlier values used with these correlation equations may be suspect. The gas−liquid critical properties of substances are also important in predicting the phase behavior of binary and multicomponent mixtures. Indeed, the development of predictive equations for mixtures has been hindered by the lack of reliable experimental or predicted pure-component critical property data. The critical properties of mixtures have been reviewed by Hicks and Young[6] and more recently in a book by Sadus.[7]

Unfortunately, the number of substances for which any critical property is known is relatively low, currently just over 400. Many of these values are quite old, and the accuracy of some of these older values is questionable. The gas−liquid critical temperatures of the chlorinated alkanes and halogenated aromatic hydrocarbons reported here are part of a project to significantly expand the existing critical property database set for pure substances and ascertain which of the older reported values are reliable. At the conclusion of the project the critical properties of at least 180 substances will have been measured. Recently, we reported the critical temperatures of 45 ethers, esters, and ketones[8] and 41 chlorinated alkanes and halogenated aromatic compounds.[9]

Reviews on the gas−liquid critical properties of pure substances have been published by Kobe and Lynn[10] (1953), Kudchadker et al.[11] (1968), Matthews[12] (1972), Ambrose and Young[13] (1995), Ambrose and Tsonopoulos[14] (1995), Gude and Teja[15] (1995), Daubert[16] (1996), Tsonopolous and Ambrose[17] (1996), Kudchadker, Ambrose, and Tsonopolous[18] (2001), and Tsonopolous and Ambrose[19] (2001). The last seven of these reviews are part of a series which aims to provide a comprehensive review of all gas−liquid critical property data reported, together with "recommended" gas−liquid critical property values for each substance.

Experimental Apparatus and Procedure

The critical temperatures were measured using the sealed-tube technique, with the substance under study occupying at room temperature one-third of the tube volume. In this work, 0.1 cm internal diameter quartz tubes of approximately 8 cm in length were used. The critical temperature was determined by heating a sample to just above its critical point, allowing it to cool slowly, and noting the temperature at which the liquid−vapor meniscus in the sealed tube reappears. The meniscus reappeared within the middle third of the tube. The error in the critical temperature data as a result of the meniscus reappearing within the middle third of the tube was estimated to be within 0.02 K. Each gas−liquid critical temperature reported in this work is the average of at least four readings carried out on at least three sample tubes containing the same substance. Where successive temperature readings made on a given sample tube differ by more than 0.1 K, only the first reading taken with each sample tube is used. A more detailed description of the method has been described elsewhere.[20,13] Care was taken to degas the samples using freeze−pump−thaw cycles with liquid nitrogen as the coolant. The presence of dissolved air in the sample tube can give rise to two effects: (i) a reaction between the sample and the dissolved air and (ii) a two-component mixtures effect, both of which can have an influence on the observed critical temperature. Note that there are also many substances which will decompose at or near the critical temperature in the absence of air. The aluminum furnace used in this work was made from a casting of approximately 35 cm in length and 15 cm in diameter. The source and purity of the chemicals used in this work are given in Table 1. The chemicals were used

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Table 1. Critical Temperatures of Alkenes, Amines, and Cyclic Hydrocarbons

name	formula	CASRN	T_c/K	ref[a]	purity[b]/mass fraction
		Alkenes			
2-methylbutene	$(CH_3)_2CHCH=CH_2$	26760-64-5	467.0 ± 0.2	(i)	0.98 (a)
2,3-dimethyl-1-butene	$(CH_3)_2CHC(CH_3)=CH_2$	563-78-0	497.7 ± 0.2	(i)	>0.98 (a)
3,3-dimethyl-1-butene	$(CH_3)_3CCH=CH_2$	558-37-2	477.4 ± 0.4	(i)	>0.98 (a)
2,3-dimethyl-2-butene	$(CH_3)_2C=C(CH_3)_2$	563-79-1	521.0 ± 0.4	(i)	>0.99 (a)
2-methyl-1-pentene	$CH_3CH_2CH_2C(CH_3)=CH_2$	763-29-1	521.0 ± 0.4	(i)	>0.99 (a)
4-methyl-1-pentene	$(CH_3)_2CHCH_2CH=CH_2$	691-37-2	493.1 ± 0.2	(i)	0.98 (a)
2-methyl-2-pentene	$CH_3CH_2CH=C(CH_3)_2$	625-27-4	509.3 ± 0.2	(i)	0.98 (a)
cis-4-methyl-2-pentene	$(CH_3)_2CHCH=CHCH_3$	691-38-3	496.3 ± 0.2	(i)	0.99 (a)
2,3-dimethyl-1-pentene	$CH_3CH_2CH(CH_3)C(CH_3)=CH_2$	3404-72-6	533.6 ± 0.3	(i)	≥0.99 (b)
4,4-dimethyl-1-pentene	$CH_2=CHCH_2C(CH_3)_3$	762-62-9	516 ± 2	(i)	≥0.99 (b)
cis-2-hexene	$CH_3CH_2CH_2CH=CHCH_3$	7688-21-3	513.4 ± 0.4	(i)	≈0.97 (b)
cis-3-hexene	$C_2H_5CH=CHC_2H_5$	7642-09-3	510.2 ± 0.6	(i)	≥0.95 (b)
trans-2-hexene	$CH_3CH_2CH_2CH=CHCH_3$	4050-45-7	509.0 ± 0.4	(i)	>0.98 (a)
trans-3-hexene	$C_2H_5CH=CHC_2H_5$	13269-52-8	507.4 ± 0.3	(i)	0.96 (a)
2-methyl-1-hexene	$CH_3(CH_2)_3C(CH_3)=CH_2$	6094-02-6	541.8 ± 0.9	(i)	>0.98 (b)
5-methyl-1-hexene	$(CH_3)_2CHCH_2CH_2CH=CH_2$	3524-73-0	528.7 ± 0.5	(i)	>0.99 (b)
cis-2-heptene	$CH_3(CH_2)_3CH=CHCH_3$	6443-92-1	548.5 ± 0.2	(i)	0.97 (a)
trans-2-heptene	$CH_3(CH_2)_3CH=CHCH_3$	14686-13-6	542.8 ± 0.2	(i)	>0.99 (a)
trans-3-heptene	$CH_3CH_2CH_2CH=CHCH_2CH_3$	14696-14-7	538.6 ± 0.2	(i)	0.99 (a)
2-methyl-1-heptene	$CH_3(CH_2)_4C(CH_3)=CH_2$	15870-10-7	567.5 ± 0.3	(i)	>0.99 (b)
2-methyl-2-heptene	$CH_3(CH_2)_3CH=C(CH_3)_2$	627-97-4	568.9 ± 0.4	(i)	≈0.98 (b)
trans-2-octene	$CH_3(CH_2)_4CH=CHCH_3$	13389-42-9	569.8 ± 0.5	(i)	≥0.99 (b)
trans-4-octene	$CH_3(CH_2)_2CH=CH(CH_2)_2CH_3$	14850-23-8	566.3 ± 0.2	(i)	≈0.99 (b)
		Amines			
1-propanamine	$CH_3CH_2CH_2NH_2$	117617-49-9	499.2 ± 0.5	(i)	>0.99 (a)
			491.2	(ii)	
			497.0	(iii)	
			497	(iv)	
2-propanamine	$(CH_3)_2CHNH_2$	75-31-0	472.5 ± 0.2	(i)	0.99 (a)
			471.8 ± 0.3	(v)	
cyclohexanamine	$C_6H_{11}NH_2$	108-91-8	626.8 ± 0.2	(i)	>0.99 (a)
hexanamine	$CH_3(CH_2)_5NH_2$	111-26-2	592.3 ± 0.4	(i)	0.99 (a)
2-heptanamine	$CH_3(CH_2)_4CH(NH_2)CH_3$	123-82-0	598.0 ± 0.3	(i)	0.99 (a)
N-methylhexanamine	$CH_3(CH_2)_5NHCH_3$	35161-70-7	592 ± 1	(i)	0.96 (a)
N-propyl-1-propanamine (dipropanamine)	$(CH_3(CH_2)_2)_2NH$	142-84-7	555.8 ± 0.5	(i)	>0.995 (b)
N-butyl-1-butanamine (dibutanamine)	$(CH_3(CH_2)_3)_2NH$	111-92-2	607.5 ± 0.5	(i)	>0.995 (b)
			607.5 ± 0.3	(vi)	
		Cyclic Hydrocarbons			
cyclohexane	C_6H_{12}	110-82-7	553.6 ± 0.5	(i)	>0.99 (c)
			553.8 ± 0.2	(vii)	
cyclooctane	C_9H_{18}	292-64-8	647.5 ± 0.5	(i)	>0.99 (a)
			647.2	(viii)	
ethylcyclohexane	$C_6H_{11}C_2H_5$	1678-91-7	606.9 ± 0.2	(i)	>0.99 (a)
propylcyclohexane	$C_6H_{11}CH_2CH_2CH_3$	1678-92-8	630.8 ± 0.4	(i)	0.99 (a)
butylcyclohexane	$C_6H_{11}(CH_2)_3CH_3$	1678-93-9	653.1 ± 0.4	(i)	>0.99 (a)
(1-methylethyl)cyclohexane (isopropylcyclohexane)	$C_6H_{11}CH(CH_3)_2$	696-29-7	632.2 ± 0.2	(i)	0.99 (a)
(2-methylpropyl)cyclohexane (isobutylcyclohexane)	$C_6H_{11}CH_2CH(CH_3)_2$	1678-98-4	642.1 ± 0.2	(i)	≥0.97 (d)
(1,1-dimethylethyl)cyclohexane (*tert*-butylcyclohexane)	$C_6H_{11}C(CH_3)_3$	3178-22-1	652.0 ± 0.2	(i)	>0.99 (a)

[a] (i) this work; (ii) Vincent and Chappius[21] (1886); (iii) Berthoud[22] (1917); (iv) Glaser and Ruland[23] (1957); (v) Kobe and Mathews[24] (1970); (vi) Toczylkin and Young[25] (1980); (vii) Daubert[16] (1996); (viii) Hicks and Young[26] (1971). [b] Source of chemical: (a) Aldrich; (b) Fluka; (c) Merck; (d) Tokyo Kasei Kogyo.

without further purification. The estimated uncertainty in the value of the critical temperature is given with the value.

Results and Discussion

Alkenes. The 23 alkenes (C_5 to C_8) studied in this work had not been previously reported. In fact, the most recent review[17] of the critical properties of unsaturated aliphatic hydrocarbons lists recommended values (based on previously reported experimental data) for only 24 alkenes and 3 alkynes. The precision of our measured alkene critical temperatures ranged from 0.2 K to 2 K.

Amines. The critical temperatures of three of the eight amines (C_3 to C_8) measured in this work have been previously reported. However, the available data are limited and many of these values are quite old. The critical temperature for 1-propanamine measured in this work is 8 K higher than the value reported by Vincent and Chappius[21] (1886), and it is about 2 K higher than the values reported by Berthoud[22] (1917) and Glaser and Ruland[23] (1957). For 2-propanamine, our value is 0.7 K higher than the one reported by Kobe and Mathews[24] (1970), while, for *N*-butyl-1-butanamine, our value agrees within experimental uncertainty with the one reported by

Toczylkin and Young[25] (1980). The precision of all the measured amine critical temperatures in this work ranged from 0.2 K to 2 K.

Cyclic Hydrocarbons. Very little experimental data are available on the critical properties of cyclic hydrocarbons. In fact, only data for 10 cyclic hydrocarbons have been previously reported.[15] The critical properties for cyclohexane have been extensively investigated. A recommended critical temperature for cyclohexane was reported by Daubert,[15] in his review on the available experimentally determined branched alkane and cycloalkane critical data. It is based on 15 experimentally determined critical temperature values and agrees with our value within 0.2 K (i.e. within experimental uncertainty).

Hicks and Young[26] are the only workers to have previously reported the critical temperature of cyclooctane. This agrees reasonably well our value, with both values being within 0.3 K of each other. The critical temperatures for the other cyclic hydrocarbons reported here have not been previously investigated.

Conclusions

The gas−liquid critical temperatures of 23 alkenes (C_5 to C_8), 8 amines (C_3−C_8), and 8 cyclic hydrocarbons (C_8−C_{10}) have been reported. Most of these substances have not had their critical temperatures measured previously. The precision with which the critical temperatures of the alkenes were determined ranged from 0.2 K to 2 K, with the precision for most values being within 0.2 K. For the amine compounds studied, precision ranged from 0.2 K to 1 K, while, for the cyclic hydrocarbons, precision was typically around 0.2 K.

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