J. Chem. Eng. Data **2000,** *45,* 437−439

The Gas−Liquid Critical Temperature of Some Chlorinated Alkanes and Halogenated Aromatic Hydrocarbons

David W. Morton*

Division of Physical Sciences and Engineering, La Trobe University, Bendigo, P.O. Box 199,
Bendigo 3550, Australia

Matthew P. W. Lui, Cam A. Tran, and Colin L. Young

School of Chemistry, University of Melbourne, Parkville 3052, Australia

The gas−liquid critical temperatures of 13 chlorinated alkanes (C_3−C_8) and 28 halogenated aromatic compounds (C_6−C_7) are reported. These values, together with the previously reported critical temperatures of about 140 other halogenated hydrocarbons, provide an extended data set which can be used to develop more accurate correlations for predicting the critical temperatures of halogenated 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 (Ambrose, 1978, 1979; Joback and Reid, 1987; Reid et al., 1987; Storvick and Sandler, 1977). 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 (1975) and more recently in a book by Sadus (1992).

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 (Morton et al., 1999). The critical temperature of 20 of the substances chosen had been measured previously. Many of the values were published 40 or more years ago and were thought to be suspect. A variation of up to 10 K was found between our values and the older data. The exception was the critical temperature values reported by Young (1910) for methyl propanoate and ethyl propanoate. These differed from our values by only 0.2 and 0.5 K, respectively.

Reviews on the gas−liquid critical properties of pure substances have been published by Kobe and Lynn (1953), Kudchadker et al. (1968), Matthews (1972), Ambrose and Young (1995), Ambrose and Tsonopoulos (1995), Gude and Teja (1995), and Tsonopolous and Ambrose (1996). The last five of these reviews are part of a series by the critical properties group of the IUPAC Commission I.2 on Thermodynamics, Subcommittee on Thermodynamic Data, 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. 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 (Young, 1978; Ambrose and Young, 1995). 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

---

* To whom correspondence should be addressed.

10.1021/je9902490 CCC: $19.00

Table 1. Critical Temperatures of Chlorinated Alkanes, Fluorinated Toluenes, and Halogenated Benzenes

name	formula	CASRN	T_c/K	ref	purity/mass fraction
	Chlorinated Alkanes				
2-chloropropane	$(CH_3)_2CHCl$	75-29-6	484 ± 1	*a*	>0.99[b]
1-chlorobutane	$CH_3(CH_2)_3Cl$	109-69-3	539.2 ± 0.3	*a*	>0.99[b]
2-chlorobutane	$CH_3CH_2CH(Cl)CH_3$	78-86-4	518.6 ± 0.3	*a*	>0.99[b]
2-chloro-2-methylpropane (*tert*-butyl chloride)	$(CH_3)_3CCl$	507-20-0	500 ± 9	*a*	0.99[b]
1-chloropentane	$CH_3(CH_2)_4Cl$	543-59-9	571.2 ± 0.2	*a*	0.99[b]
2-chloro-2-methylbutane (*tert*-amyl chloride)	$CH_3CH_2C(CH_3)_2Cl$	594-36-5	509.1 ± 0.3	*a*	0.98[b]
1,2-dichloropropane	$CH_3CH(Cl)CH_2Cl$	78-87-5	578.5 ± 2	*a*	0.99[b]
1,3-dichloropropane	$Cl(CH_2)_3Cl$	142-28-9	614.6 ± 2	*a*	0.99[b]
1-chlorohexane	$CH_3(CH_2)_5Cl$	544-10-5	599 ± 2	*a*	0.99[b]
3-chloro-3-methylpentane	$CH_3C(CH_2CH_3)_2Cl$	918-84-3	528 ± 2	*a*	0.99[b]
1-chloroheptane	$CH_3(CH_2)_6Cl$	629-06-1	614 ± 6	*a*	0.99[b]
1-chlorooctane	$CH_3(CH_2)_7Cl$	111-85-3	643 ± 1	*a*	0.99[b]
chlorocyclohexane	$C_6H_{11}Cl$	542-18-7	586 ± 1	*a*	0.99[b]
	Fluorinated Toluenes				
2-fluorotoluene (*o*-fluorotoluene)	$CH_3C_6H_4F$	95-52-3	591.2 ± 0.2	*a*	≥0.97[c]
3-fluorotoluene (*m*-fluorotoluene)	$CH_3C_6H_4F$	352-70-5	591.8 ± 0.2	*a*	≥0.97[c]
4-fluorotoluene (*p*-fluorotoluene)	$CH_3C_6H_4F$	352-32-9	592.1 ± 0.4	*a*	≥0.97[c]
2,4-difluorotoluene	$CH_3C_6H_3F_2$	452-76-6	581.4 ± 0.2	*a*	≥0.97[c]
2,5-difluorotoluene	$CH_3C_6H_3F_2$	452-67-5	587.8 ± 0.2	*a*	≥0.97[c]
2,6-difluorotoluene	$CH_3C_6H_3F_2$	443-84-5	581.8 ± 0.2	*a*	≥0.97[c]
3,4-difluorotoluene	$CH_3C_6H_3F_2$	2927-34-6	598.5 ± 0.2	*a*	≥0.97[c]
	Halogenated Benzenes				
chlorobenzene	C_6H_5Cl	108-90-7	633.4 ± 0.3	*a*	0.998[b]
			635.4	*d*	
			632.4 ± 0.1	*e*	
1,3-dichlorobenzene	$C_6H_4Cl_2$	541-73-1	685.7 ± 0.2	*a*	0.98[b]
1-bromo-2-fluorobenzene (*o*-bromofluorobenzene)	BrC_6H_4F	1072-85-1	669.6 ± 0.3	*a*	≥0.97[c]
1-bromo-3-fluorobenzene (*m*-bromofluorobenzene)	BrC_6H_4F	1073-06-9	652.0 ± 0.2	*a*	≥0.97[c]
1-bromo-4-fluorobenzene (*p*-bromofluorobenzene)	BrC_6H_4F	460-00-4	654.8 ± 0.2	*a*	≥0.97[c]
1-chloro-2-fluorobenzene (*o*-chlorofluorobenzene)	ClC_6H_4F	348-51-6	633.8 ± 0.2	*a*	≥0.97[c]
1-chloro-3-fluorobenzene (*m*-chlorofluorobenzene)	ClC_6H_4F	625-98-9	615.9 ± 0.2	*a*	≥0.97[c]
1-chloro-4-fluorobenzene (*p*-chlorofluorobenzene)	ClC_6H_4F	352-33-0	620.1 ± 0.2	*a*	≥0.97[c]
1,2-difluorobenzene (*o*-difluorobenzene)	$C_6H_4F_2$	367-11-3	566.0 ± 0.2	*a*	≥0.97[c]
1,3-difluorobenzene (*m*-difluorobenzene)	$C_6H_4F_2$	372-18-9	548.4 ± 0.2	*a*	≥0.97[c]
1,4-difluorobenzene (*p*-difluorobenzene)	$C_6H_4F_2$	540-36-3	556.9 ± 0.2	*a*	≥0.97[c]
			556 ± 2	*f*	
1-chloro-2,4-difluorobenzene	$ClC_6H_3F_2$	1435-44-5	609.6 ± 0.2	*a*	≥0.97[c]
1-chloro-2,5-difluorobenzene	$ClC_6H_3F_2$	2367-91-1	612.5 ± 0.2	*a*	≥0.97[c]
1-chloro-3,4-difluorobenzene	$ClC_6H_3F_2$	696-02-6	609.2 ± 0.2	*a*	≥0.97[c]
1-chloro-3,5-difluorobenzene	$ClC_6H_3F_2$	1435-43-4	592.0 ± 0.2	*a*	≥0.97[c]
1,2,3-trifluorobenzene	$C_6H_3F_3$	1489-53-8	560.3 ± 0.2	*a*	≥0.97[c]
1,2,4-trifluorobenzene	$C_6H_3F_3$	367-23-7	551.1 ± 0.2	*a*	≥0.97[c]
1,3,5-trifluorobenzene	$C_6H_3F_3$	372-38-3	530.9 ± 0.2	*a*	≥0.97[c]
2-bromobenzotrifluoride (*o*-bromobenzotrifluoride)	$BrC_6H_4CF_3$	392-83-6	656.5 ± 0.2	*a*	≥0.97[c]
3-bromobenzotrifluoride (*m*-bromobenzotrifluoride)	$BrC_6H_4CF_3$	401-78-5	627.1 ± 0.2	*a*	≥0.97[c]
4-bromobenzotrifluoride (*p*-bromobenzotrifluoride)	$BrC_6H_4CF_3$	402-43-7	629.8 ± 0.2	*a*	≥0.97[c]

[a] This work. [b] Aldrich. [c] Fluorochem. [d] Altschul, 1893. [e] Young, 1910. [f] Jockers and Schneider, 1978.

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 without further purification.

Results and Discussion

Chlorinated Alkanes. The precision with which the critical temperatures of chlorinated alkanes were determined ranged from 0.2 K (1-chloropentane) to 9 K (2-chloro-2-methylpropane). However, the precision of most measurements was within 2 K. The cause of variation in stability of these substances when heated is uncertain but may be due to traces of oxygen remaining in the sample tube and/or impurities present in the samples used, reacting with the chloroalkanes at or near their critical temperatures. As expected, an increase in the degree of branching in the carbon chain for a chloroalkane results in a decrease in the critical temperature. For example, 1-chlorobutane (T_c = 539.2 K) has a higher critical temperature than 2-chlorobutane (T_c = 518.6 K).

Figure 1 gives a plot of critical temperature vs carbon number for a homologous series of C_1-C_8 1-chloroalkanes (C_4-C_8 1-chloroalkanes, our work) and C_1-C_8 alkanes (Ambrose and Tsonopolous, 1995). The smooth curves in Figure 1 are best fits of the measured data. Even though the values for 1-chloroethane and 1-chloropropane (Berthoud, 1917) are over 80 years old, they appear to be in general agreement with our data and the recent value reported for chloromethane by Mansoorian et al. (1981). The curve of best fit indicates that the actual value for 1-chloroheptane may lie about 6 K higher than the one reported here. An uncertainty of ±6 K in the determination of the critical temperature for 1-chloroheptane indicates the value is not as reliable as the other values in the 1-chloroalkane data set. Figure 1 shows for a given number of carbon atoms that the 1-chloroalkane molecule has a

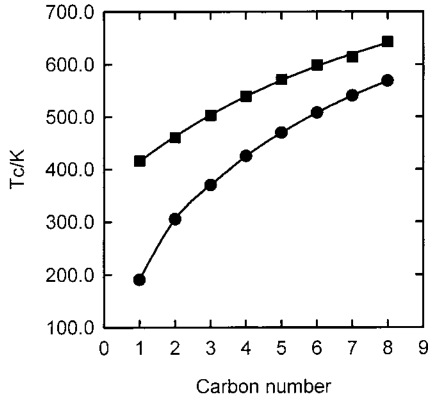

Figure 1. Plot of critical temperature T_c vs carbon number for a homologous series of (a) 1-chloroalkanes (■) and (b) *n*-alkanes (●).

higher critical temperature than its corresponding alkane. Note that, as the number of carbon atoms increases, the difference in the critical temperature between the 1-chloroalkane molecule and its corresponding alkane decreases.

Fluorinated Toluenes. The fluorinated toluenes studied remained stable while their gas−liquid critical temperatures were determined. The precision to which the critical temperatures of fluorinated toluenes were measured ranged from 0.2 K (2-fluorotoluene) to 0.4 K (4-fluorotoluene). The critical temperatures of the three monofluorinated toluenes are very similar. However, the critical temperature increases slightly (0.9 K) as the fluorine atom attached to the benzene ring moves further away from the methyl group, i.e., T_c(ortho) < T_c(meta) < T_c(para). The critical temperatures of the difluorotoluenes vary over a range of 17 K, from 581.4 K for 2,4-difluorotoluene to 598.5 K for 3,4-difluorotoluene.

Halogenated Benzenes. In general, the halogenated benzene compounds studied remained stable during the measurement of their gas−liquid critical temperatures, with the uncertainty between measurements for a given compound being generally less than 0.3 K and typically around 0.2 K. For the three difluorobenzene isomers, T_c(meta) < T_c(para) < T_c(ortho). The critical temperatures of the difluorobenzenes vary over a range of 18 K, from 548.4 K for 1,3-difluorobenzene to 566.0 K for 1,2-difluorobenzene. For a given difluorobenzene isomer, replacement of one of the fluorine atoms with a chlorine atom results in an increase in the critical temperature of the compound. Subsequent replacement of the chlorine atom with a bromine atom results in a further increase in the critical temperature, e.g., T_c(1,2-difluorobenzene) < T_c(1-chloro-2-fluorobenzene) < T_c(1-bromo-2-difluorobenzene).

Conclusion

The gas−liquid critical temperatures of 13 chlorinated alkanes (C_3−C_8) and 28 halogenated aromatic compounds (C_6−C_7) have been reported. Most of these halogenated hydrocarbons have not had their critical temperatures measured previously. The precision with which the critical temperatures of chlorinated alkanes were determined ranged from 0.2 K (1-chloropentane) to 9 K (2-chloro-2-methylpropane), with the precision of most values being within 2 K. Higher precision measurements were obtained for the halogenated aromatic compounds studied. For fluorinated toluenes, uncertainties ranged from 0.2 K (2-fluorotoluene) to 0.4 K (4-fluorotoluene). For fluorinated benzene compounds, the uncertainty between measurements for a given compound was generally less than 0.3 K and typically around 0.2 K.

Literature Cited

Altschul, M. Über die kritischen Grössen einiger organischen Verbindungen. *Z. Phys. Chem.* **1893**, *11*, 577−597.

Ambrose, D. *Correlation and Estimation of Vapour−Liquid Critical Properties: I. Critical Temperatures of Organic Compounds*; National Physical Laboratory: Teddington, U.K., 1978.

Ambrose, D. *Correlation and Estimation of Vapour−Liquid Critical Properties: II. Critical Pressures and Critical Volumes of Organic Compounds*; National Physical Laboratory: Teddington, U.K., 1979.

Ambrose, D.; Tsonopolous, C. Vapour−Liquid Critical Properties of Elements and Compounds. 2. Normal Alkanes. *J. Chem. Eng. Data* **1995**, *40*, 531−546.

Ambrose, D.; Young, C. L. Vapour−Liquid Critical Properties of Elements and Compounds. 1. An Introductory Survey. *J. Chem. Eng. Data* **1995**, *40*, 345−357.

Berthoud, A. Determinations of Critical Temperatures and Pressures of Amines and Alkyl Chlorides. *J. Chim. Phys.* **1917**, *15*, 3−29.

Gude, M.; Teja, A. S. Vapour−Liquid Critical Properties of Elements and Compounds. 4. Aliphatic Alkanols. *J. Chem. Eng. Data* **1995**, *40*, 1025−1036.

Hicks, C. P.; Young, C. L. The Gas−Liquid Critical Properties of Binary Mixtures. *Chem. Rev.* **1975**, *75*, 119−175.

Joback, K. G.; Reid, R. C. Estimation of Pure-Component Properties From Group Contributions. *Chem. Eng. Commun.* **1987**, *57*, 233−243.

Jockers, R.; Schneider, G. M. Fluid Mixtures at High Pressures. Fluid Phase Equilibria in the Systems Fluorobenzene + Water, 1,4-Difluorobenzene + Water, and 1,2,3,4-Tetrahydronaphthalene + Decahdyronaphthalene (trans) + Water up to 360 MPa. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 576−582.

Kobe, K. A.; Lynn, R. E., Jr. The Critical Properties of Elements and Compounds. *Chem. Rev.* **1953**, *52*, 117−236.

Kudchadker, A. P.; Alani, G. H.; Zwolinski, B. J. The Critical Constants of Organic Substances. *Chem. Rev.* **1968**, *68*, 659−735.

Mansoorian, H.; Hall, K. R.; Holste, J. C.; Eubank, P. T. The Density of Gaseous Ethane and of Fluid Methyl Chloride and the Vapour Pressure of Methyl Chloride. *J. Chem. Thermodyn.* **1981**, *13*, 1001−1021.

Matthews, J. F. The Critical Constants of Inorganic Substances. *Chem. Rev.* **1972**, *72*, 71−100.

Morton, D. W.; Lui, M.; Young, C. L. The gas−liquid critical temperatures of some ethers, esters and ketones. *J. Chem. Thermodyn.* **1999**, *31*, 675−684.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.

Sadus, R. J. *High Pressure Phase Behaviour of Multicomponent Fluid Mixtures*; Elsevier: Amsterdam, The Netherlands, 1992.

Storvick, T. S., Sandler, S. I., Eds. *Phase Equilibria and Fluid Properties in the Chemical Industry*; American Chemical Society: Washington, DC, 1977.

Tsonopolous, C.; Ambrose, D. Vapour−Liquid Critical Properties of Elements and Compounds. 6. Unsaturated Aliphatic Hydrocarbons. *J. Chem. Eng. Data* **1996**, *41*, 645−656.

Young, S. The Vapour-Pressures, Specific Volumes, Heats of Vaporisation, and Critical Constants of Thirty Pure Substances. *Sci. Proc. R. Dublin Soc.* **1909−10**, *12*, 374−443.

Young, C. L. Chapter 3. In *Experimental Methods for Studying Phase Behaviour of Mixtures at High Temperatures and Pressures*; McGlashan, M. L., Ed.; Specialist Periodical Reports, Chemical Thermodynamics; The Chemical Society: London, 1978; Vol. 2.

Received for review September 9, 1999. Accepted January 17, 2000. This work is part of a project on the critical properties of organic substances for plant design supported financially by the Australian Research Council.

JE9902490