Critical-Point Measurements for Nine Compounds by a Flow Method

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Critical-point measurements consisting of critical temperatures and critical pressures by a flow method have been made on nine compounds: ethanenitrile, 1-phenylethanol, 1,3-propanediol, 1-*n*-propoxy-2-propanol, 1-*n*-butoxy-2-propanol, bis(2-aminoethyl)amine, diethyl sulfide, 1,2-ethanediol, and 1,2-propanediol.

Introduction

This work is part of an ongoing investigation of the critical properties for compounds selected for industrial interest in 1995 and 1996 by sponsors of Project 851 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. This paper reports experimental measurements of the critical properties for nine compounds studied in a flow apparatus. Some of these compounds showed moderate degradation while others showed rapid degradation with time. Measurements were also attempted on 1-dodecanethiol and 5-ethylidene-2-norbornene. These compounds degraded so quickly that measurements were not possible in this apparatus.

Experimental Section

The flow apparatus and procedures used for these measurements have been described earlier (Wilson et al., 1995). The only significant change in procedure was the use of distillation rather than a drying agent to remove water from the compounds. The water content of all of the compounds was determined by Karl Fischer titration. The ITS-90 temperature scale was used for these measurements.

Results and Discussion

Table 1 presents the measured critical-point properties for the nine compounds included in this study. This table reports the critical temperature and pressure for each compound. Where available, values are compared with values from the literature.

The reported critical temperature and critical pressure were obtained by extrapolating the measured values at three or four average residence times to zero residence time. The extrapolation was either a linear or quadratic fit of the measured data. The reliability of the extrapolation depended on the slope and curvature of the resulting equation. For compounds such as 1-*n*-butoxy-2-propanol, ethanenitrile, diethyl sulfide, and 1-*n*-propoxy-2-propanol, the extrapolating equation had minimal slope and curvature, resulting in a reliable extrapolation. Figures 1 and 2 show the plots for ethanenitrile to illustrate this process. The other compounds had varying degrees of slope and curvature which were figured into the stated accuracy for each measurement. Examples of these extrapolations are given in Figures 3−6 for 1,2-propanediol and 1,2-ethanediol.

Table 1. Results of Critical Measurements

compound	data source	T_c/K	P_c/MPa
ethanenitrile	this work	545.6 ± 0.1	4.884 ± 0.006
	Rodriguez and McLure (1979)	545.5 ± 0.3	4.83 ± 0.02
1-phenylethanol	this work	699 ± 2	3.77 ± 0.07
1,3-propanediol	this work	722 ± 4	6.3 ± 0.6
1-*n*-propoxy-2-propanol	this work	605.1 ± 0.2	3.051 ± 0.005
1-*n*-butoxy-2-propanol	this work	624.9 ± 0.1	2.739 ± 0.001
bis(2-aminoethyl)amine	this work	709 ± 6	4.3 ± 0.4
diethyl sulfide	this work	557.8 ± 0.1	3.897 ± 0.001
	Daubert et al. (1995)	557 ± 5	3.96 ± 0.08
1,2-ethanediol	this work	719 ± 6	8.2 ± 0.4
	Teja and Anselme (1990)	718 ± 9	
	Nikitin et al. (1993)	720 ± 7	8.2 ± 0.3
1,2-propanediol	this work	676.4 ± 0.3	5.941 ± 0.007

Critical values were found in the literature for diethyl sulfide, 1,2-ethanediol, and ethanenitrile. The critical temperature of ethanenitrile agrees with the value by Rodriguez and McLure to (1979) ±0.1 K. The critical pressure of ethanenitrile in this work is 1.1% higher than that reported by Rodriguez and McLure (1979). The results of this work for 1,2-ethanediol agree with the previous work to within the stated limits of accuracy (Teja and Anselme, 1991; Nikitin et al., 1993). Measurements on diethyl sulfide are in agreement with the values from the DIPPR 801 compilation (Daubert et al., 1995).

1-Dodecanethiol and 5-ethylidene-2-norbornene degraded so quickly that reliable measurements were not possible

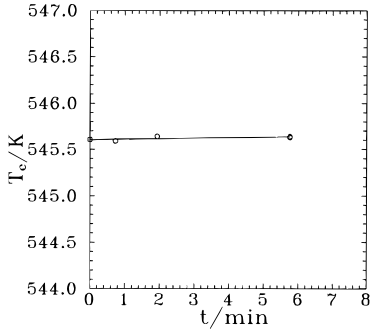

Figure 1. Critical temperature of ethanenitrile versus average residence time: (○) observed critical temperature; (—) linear fit to observed critical temperatures; (□) extrapolated critical temperature at zero residence time.

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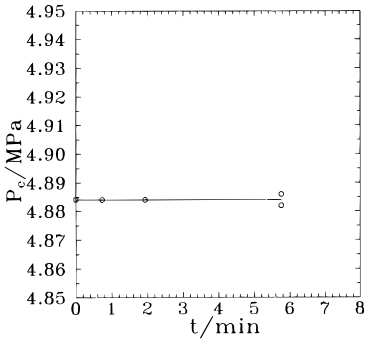

Figure 2. Critical pressure of ethanenitrile versus average residence time: (○) observed critical pressure; (—) linear fit to observed critical pressures; (G) extrapolated critical pressure at zero residence time.

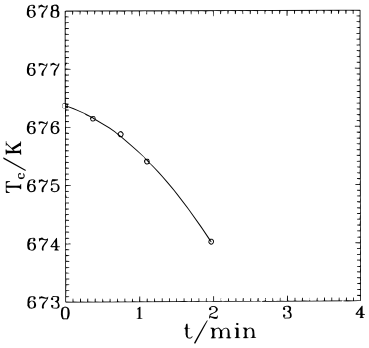

Figure 3. Critical temperature of 1,2-propanediol versus average residence time: (○) observed critical temperature; (—) quadratic fit to observed critical temperatures; (□) extrapolated critical temperature at zero residence time.

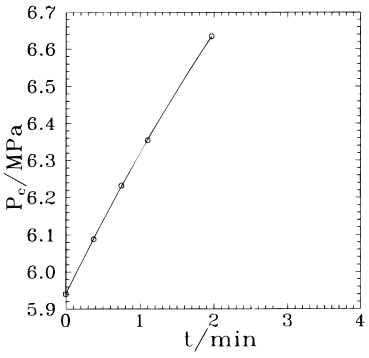

Figure 4. Critical pressure of 1,2-propanediol versus average residence time: (○) observed critical pressure; (—) quadratic fit to observed critical pressures; (□) extrapolated critical pressure at zero residence time.

in this apparatus. It was observed that 5-ethylidene-2-norbornene reacted quite exothermically above 650 K. Caution is advised if research is undertaken with this compound above approximately 600 K.

Table 2 reports measured purities and water content for the compounds studied in this work. All chemicals were purchased at the highest purity commercially available at the time these measurements were made. Water and dissolved gases were removed by distilling off a small amount of material under vacuum, but no further attempts were made to purify the chemicals. The supplier and CASRN of each chemical are also listed.

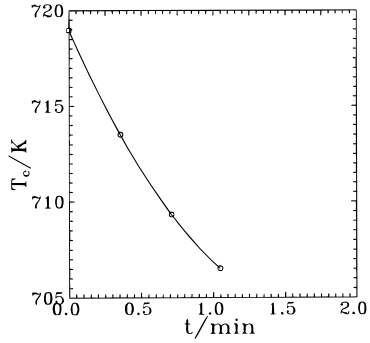

Figure 5. Critical temperature of 1,2-ethanediol versus average residence time: (○) observed critical temperature; (—) quadratic fit to observed critical temperatures; (□) extrapolated critical temperature at zero residence time.

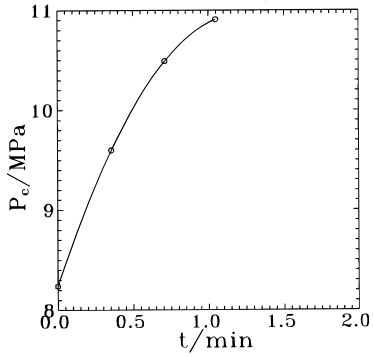

Figure 6. Critical pressure of 1,2-ethanediol versus average residence time: (○) observed critical pressure; (—) quadratic fit to observed critical pressures; (□) extrapolated critical pressure at zero residence time.

Table 2. Purity of Materials Used in Critical-Point Measurements

		analyzed purity/mass %			
compound	CASRN	this work	supplier	water/ mass %	supplier
ethanenitrile	75-05-8	99.97	99.9	0.02	Aldrich
1-phenylethanol	98-85-1	97.6	98	0.009	Alfa
1,3-propanediol	504-63-2	99.5	98	0.006	Aldrich
1-*n*-propoxy-2-propanol	1569-01-3	99.9[a]	99	0.03	Aldrich
1-*n*-butoxy-2-propanol	5131-66-8	96.9[b]	99	0.0056	Aldrich
bis(2-aminoethyl)amine	111-40-0	99.4	99	0.09[c]	Aldrich
diethyl sulfide	352-93-2	98.6	98	0.0360	Acros
1,2-ethanediol	107-21-1	99+[d]	99.8	0.0031	Aldrich
1,2-propanediol	57-55-6	99+[d]	99.5	0.0096	Aldrich

[a] This compound was a mixture of two isomers: 1-*n*-propoxy-2-propanol and 2-*n*-propoxy-1-propanol. The isomers eluted too closely together to be resolved by gas chromatographic (GC) analysis, and only one principal peak was observed. The supplier stated that a typical lot contains 95% 1-*n*-propoxy-2-propanol and 5% 2-*n*-propoxy-1-propanol. [b] The predominant impurity was 2-*n*-butoxy-1-propanol at 2.8%. [c] The reported water analysis for bis(2-aminoethyl)amine was measured on a lot obtained from Aldrich in 1999. [d] Only peak detected by GC analysis.

Conclusion

Reliable critical properties have been determined for nine compounds of industrial significance. These data are also useful in evaluating the applicability of current predictive techniques as well as in developing better correlations for estimating critical temperatures and pressures.

Acknowledgment

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