Critical Point Measurements for Fourteen Compounds by a Static Method and a Flow Method

Loren C. Wilson,* Howard L. Wilson, W. Vincent Wilding, and Grant M. Wilson

Wiltec Research Company, Inc., 488 South 500 West, Provo, Utah 84601

A static method was used to measure the critical temperature, critical pressure, and critical volume on three compounds: ethyl thioacetate, methoxybenzene, and 2-methoxyethanol. A flow method was used to measure the critical temperature and critical pressure on eleven compounds: acrylonitrile, 1,4-butanediol, 2-(2-butoxyethoxy)ethyl acetate, γ-butyrolactone, cyclohexanol, 1,2-ethanediamine, 2-(2-ethoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethyl acetate, 1-methoxy-2-propanol, 2-(2-methoxyethoxy)ethanol, and 2-nonanone.

Introduction

This work is part of an ongoing investigation of the critical properties for compounds selected for industrial interest in 1993 and 1994 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 fourteen compounds. Three compounds (ethyl thioacetate, methoxybenzene, and 2-methoxyethanol) were studied in a static apparatus in which the critical temperature, critical pressure, and critical volume were determined. Eleven compounds were studied in a flow apparatus in which the critical temperature and critical pressure were measured.

The three chemicals studied in the static apparatus showed slight degradation with time during the critical point measurements. Of the eleven compounds studied in the flow apparatus, some showed moderate degradation with time while others showed rapid degradation. Measurements were attempted on three additional compounds: 1,4-dichlorobutane, 2-[(2-aminoethyl)amino]ethanol, and phenyl acetate. These compounds degraded so quickly that measurements were not possible even in the flow apparatus.

Experimental Section

The static and 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 1,4-butanediol, 2-(2-butoxyethoxy)ethyl acetate, 1,2-ethanediamine, 2-(2-ethoxyethoxy)ethyl acetate, 2-(2-methoxyethoxy)ethanol, and 1-methoxy-2-propanol. The other eight compounds were dried by contacting them with 4 Å molecular sieves. The water content of all of the compounds except 1,2-ethanediamine was determined by Karl Fisher titration. Due to the basic nature of 1,2-ethanediamine, its water content could not be determined directly by Karl Fisher titration.

The ITS-90 temperature scale was used for these measurements.

Results and Discussion

Table 1 presents the measured critical point properties for the fourteen compounds included in this study. This table reports the critical temperature and pressure for each compound. The critical molar volume is also given for compounds measured in the static apparatus. Where available, values are compared with values from the literature.

Ethyl thioacetate, methoxybenzene, and 2-methoxyethanol were studied in the static apparatus. These materials showed slight to moderate degradation with time during the critical point measurements. Measurements were taken over a period of 60 to 90 min and the critical temperature and pressure were determined by extrapolating back to zero residence time in the cell. An example of this is given in Figures 1 and 2, which plot the critical temperature and pressure of methoxybenzene as a function of time. The critical properties of this compound changed quite linearly with time and the critical properties at zero residence time appear to be reliably extrapolated.

Glaser and Rüland (1957) reported measurements of the critical temperature and critical pressure for methoxybenzene. Their reported critical temperature is 4.4 K lower and their reported critical pressure is 0.04 MPa lower than measured in this work. Their method was based upon identifying the apparent discontinuity in the plot of $\log_e(p/p°)$ against $1/T$ rather than a visual observation of the critical point. That method is less sensitive than the method employed in this work. It is also unclear from their article whether the effect of decomposition was accounted for. Ambrose et al. (1974) also report a critical temperature and critical pressure for methoxybenzene. They used a sealed ampule and minimized the time required to perform an observation of the critical point. Their reported values for methoxybenzene agree with this work within the given experimental uncertainties.

The other eleven compounds were studied in the flow apparatus. Some showed moderate degradation with time, while others showed rapid degradation. 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. For several compounds, this could be done quite reliably. The extrapolation for other compounds was less certain. This uncertainty is reflected in the values reported in Table 1. Figures 3 and 4 show plots of the critical temperature and critical pressure as a function of residence time for 1,4-butanediol. Although the critical temperature and pressure changed significantly as a function of residence time, the values at zero residence time appear to be calculated reliably due to the linearity of the data. In contrast, the data for 2-(2-butoxyethoxy)ethyl acetate are presented in Figures 5 and 6. There is distinct curvature in the value of the critical property as a function of residence time. This curvature introduces greater uncertainty in the extrapolated values.

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Table 1. Results of Critical Point Measurements

compound	data source	T_c/K	P_c/MPa	V_c/L·mol^{-1}	ρ_c/kg·mL^{-3}
acrylonitrile	this work, flow	540.± 1	4.660 ± 0.014		
1,4-Butanediol	this work, flow	727 ± 2	6.22 ± 0.14		
2-(2-butoxyethoxy)ethyl acetate	this work, flow	681 ± 2	3.15 ± 0.14		
γ-butyrolactone	this work, flow	731.0 ± 0.2	5.131 ± 0.034		
cyclohexanol	this work, flow	647.1 ± 0.1	4.401 ± 0.021		
	Ambrose and Ghiassee	650.0 ± 2	4.26 ± 0.05		
	Glaser and Rüland	625	3.75		
1,2-ethanediamine	this work, flow	613.1 ± 0.2	6.707 ± 0.0.007		
2-(2-ethoxyethoxy)ethanol	this work, flow	670 ± 3	3.167 ± 0.021		
2-(2-ethoxyethoxy)ethyl acetate	this work, flow	663 ± 2	2.73 ± 0.14		
ethyl thioacetate	this work, static	590.55 ± 0.1	4.075 ± 0.069	0.319 ± 0.006	327 ± 6
methoxybenzene	this work, static	646.1 ± 0.1	4.222 ± 0.014	0.341 ± 0.007	317 ± 7
	Ambrose et al.	645.6 ± 0.5	4.25 ± 0.05		
	Glaser and Rüland	641.7	4.18		
2-methoxyethanol	this work, static	597.6 ± 0.1	5.285 ± 0.014	0.263 ± 0.005	289 ± 5
2-(2-methoxyethoxy)ethanol	this work, flow	672 ± 1	3.67 ± 0.10		
1-methoxy-2-propanol	this work, flow	579.8 ± 0.2	4.113 ± 0.007		
2-nonanone	this work, flow	651.9 ± 0.1	2.482 ± 0.007		
	Pulliam et al.	652.5 ± 0.2		0.568 ± 0.007	250 ± 3

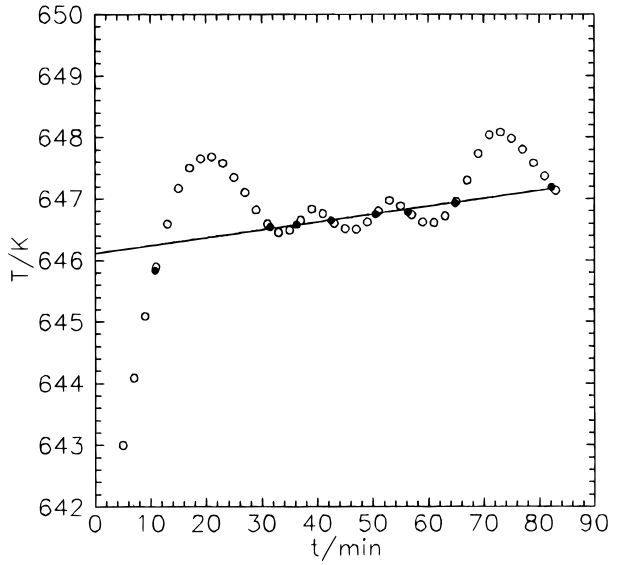

Figure 1. Critical temperature of methoxybenzene versus time: (○) temperature as a function of time; (●) observed critical temperature; (—) linear fit to observed critical temperatures.

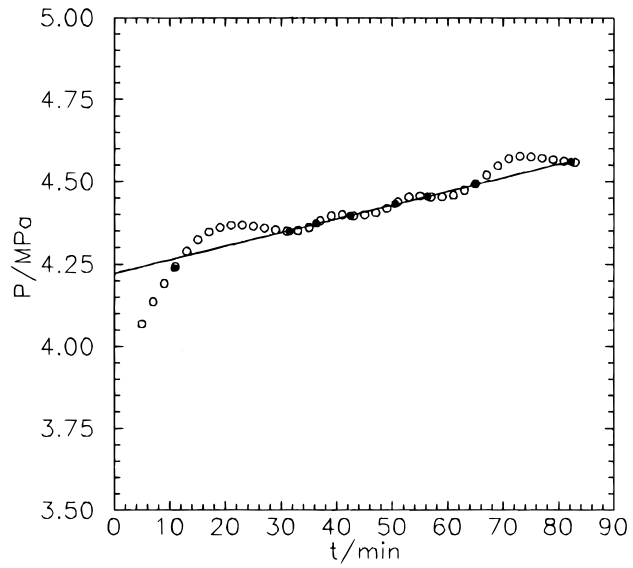

Figure 2. Critical pressure of methoxybenzene versus time: (○) pressure as a function of time; (●) observed critical pressure; (—) linear fit to observed critical pressures.

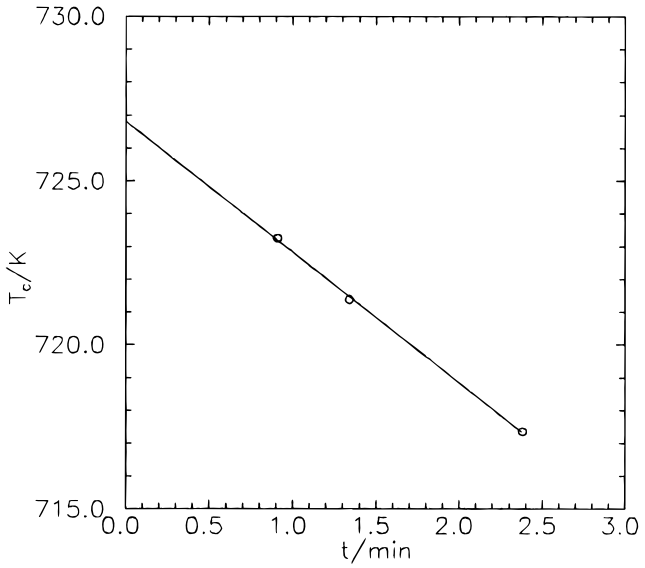

Figure 3. Critical temperature of 1,4-butanediol versus average residence time: (○) observed critical temperature; (—) linear fit to observed critical temperatures.

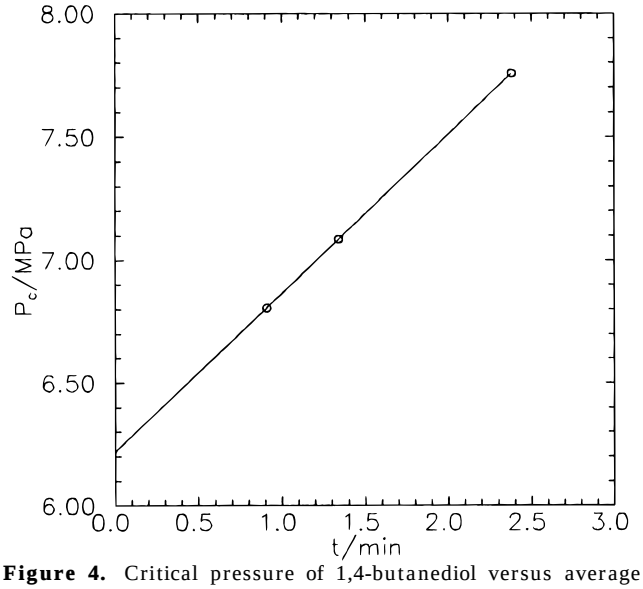

Figure 4. Critical pressure of 1,4-butanediol versus average residence time: (○) observed critical pressure; (—) linear fit to observed critical pressures.

Ambrose and Ghiassee (1987) and Glaser and Rüland (1957) report values for cyclohexanol. Ambrose and Ghiassee used a sealed ampule method and also measured the change in the observed critical temperature and pressure with time. This information was used to extrapolate the critical properties back to the unreacted material. The method of Glaser and Rüland is described above. Ambrose and Ghiassee and the current authors both observed that the apparent critical temperature of cyclohexanol decreased with time. This work is in good agreement with Ambrose

Table 2. Purity of Materials Used in Critical Point Measurements

compound (CASRN)	analyzed purity/mass % this work	analyzed purity/mass % supplier	water/mass %	supplier
acrylonitrile (107-13-1)	99.8[a]	99.9	0.05[b]	Aldrich
2-[(2-aminoethyl)amino]ethanol (929-06-6)		98.	c	Aldrich
1,4-butanediol (110-63-4)	99.7		0.028	Aldrich
2-(2-butoxyethoxy)ethyl acetate (124-17-4)	99.7		0.015	Aldrich
γ-butyrolactone (96-48-0)	99.94	99.7	0.017	Aldrich
cyclohexanol (108-93-0)	99.95	99.9	0.05[b]	Aldrich
1,4-dichlorobutane (110-56-5)	98.3	99.		Aldrich
1,2-ethanediamine (107-15-3)	99.9		c	Aldrich
2-(2-ethoxyethoxy)ethanol (111-90-0)	99.8	99.9	0.038	Aldrich
2-(2-ethoxyethoxy)ethyl acetate (112-15-2)	99.0		0.033	Aldrich
ethyl thioacetate (625-60-5)	98.6		0.05[b]	Phillips
methoxybenzene (100-66-3)	99.9		0.010	Aldrich
2-methoxyethanol (109-86-4)	99.9		0.0024	Aldrich
2-(2-methoxyethoxy)ethanol (111-77-3)	99.9	99.9	0.065	Aldrich
1-methoxy-2-propanol (107-98-2)	99.9		0.015	Aldrich
2-nonanone (821-55-6)	99.91	99.9	0.083	Aldrich
phenyl acetate (122-79-2)		99.	0.018	Aldrich

[a] Approximately 0.1 wt % inhibitor (methylhydroquinone) was added to acrylonitrile for the critical point measurements. [b] Dried using 4 Å molecular sieves. This is the average water content of other compounds dried by the same method. [c] Due to the basic nature of this compound, it could not be analyzed directly for water content by Karl Fisher titration.

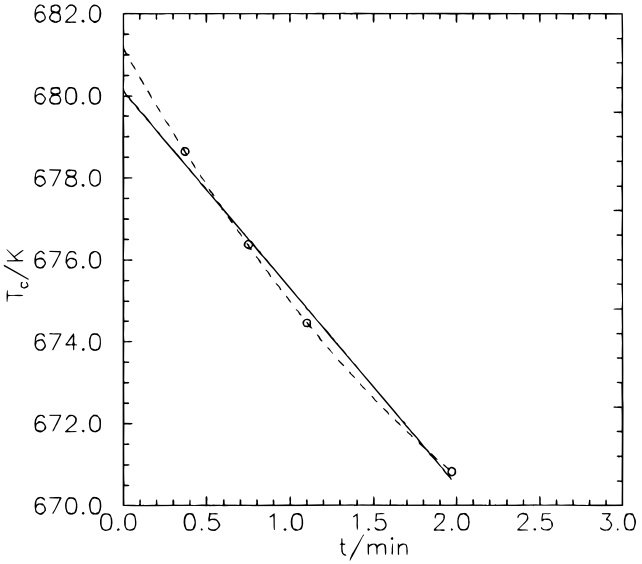

Figure 5. Critical temperature of 2-(2-butoxyethoxy)ethyl acetate versus average residence time: (○) observed critical temperature; (—) linear fit to observed critical temperatures; (- - -) quadratic fit to observed critical temperatures.

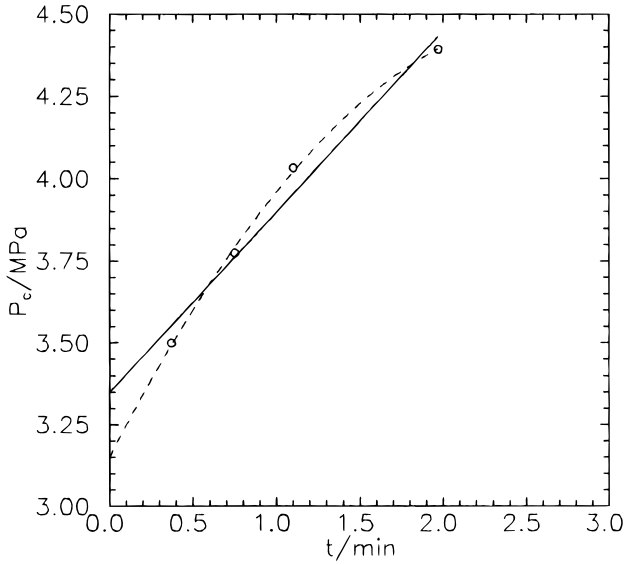

Figure 6. Critical pressure of 2-(2-butoxyethoxy)ethyl acetate versus average residence time: (○) observed critical pressure; (—) linear fit to observed critical pressures; (- - -) quadratic fit to observed critical pressures.

and Ghiassee, while Glaser and Rüland's values may show the effect of decomposition on the observed critical temperature.

Pulliam and co-workers (1994) measured the critical temperature and critical density of 2-nonanone by the sealed ampule method. They also took into account the change in the observed critical properties as a function of time. Their measured critical temperature is in good agreement with the value reported in this work.

1,4-Dichlorobutane, 2-[(2-aminoethyl)amino]ethanol, and phenyl acetate degraded so quickly that measurements were not possible even in the flow apparatus. The windows of the visual cell were very quickly rendered opaque by the degradation products of these three compounds even at the highest flow rate.

Table 2 reports measured purities and water content for the compounds studied in this work.

Conclusion

Reliable critical properties have been determined for fourteen 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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Literature Cited

Ambrose, D.; Ghiassee, N. B. Vapor pressures and critical temperatures and critical pressures of C_5 and C_6 cyclic alcohols and ketones. *J. Chem. Thermodyn.* **1987**, *19*, 903−909.

Ambrose, D.; Broderick, B. E.; Townsend, R. The critical temperature and pressure of thirty organic compounds. *J. Appl. Chem. Biotechnol.* **1974**, *24*, 359−372.

Glaser, F.; Rüland, H. *Chem.-Ing.-Tech.* **1957**, *29*, 772.

Pulliam, M. K.; Gude, M. T.; Teja, A. S. In *Experimental Results for DIPPR 1990−1991 Projects on Phase Equilibria and Pure Component Properties*; Cunningham, J. R., Jones, D. K., Eds.; DIPPR Data Series No. 2; American Institute of Chemical Engineers: New York, 1994; pp 184−187.

Wilson, L. C.; Wilding, W. V.; Wilson, H. L.; Wilson, G. M. Critical Point Measurements by a New Flow Method and a Traditional Static Method. *J. Chem. Eng. Data* **1995**, *40*, 765−768.

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