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Critical Point Measurements by a New Flow Method and a Traditional Static Method

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A new flow method and a traditional static method have been employed to obtain the critical temperatures and pressures for 11 compounds: 1,1-dimethylpropyl methyl ether, 1,1-dimethylethyl ethyl ether, toluene, ethylbenzene, (1-methylethyl)benzene, 1-methylethyl ethanoate, 2-pentanone, 2-hexanone, 2-heptanone, hexafluoroethane, and propene. Accurate critical densities were also obtained using a static method. The critical properties of stable compounds appear to be accurately determined by both methods. The flow method allows the determination of accurate critical properties for more reactive or thermally unstable compounds.

Introduction

Project 851 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers has sponsored this research to measure critical constants of various compounds of industrial importance. The critical constants of 11 compounds have been measured. 1,1-Dimethylpropyl methyl ether (TAME), 1,1-dimethylethyl ethyl ether (ETBE), toluene, ethylbenzene, (1-methylethyl)benzene, 1-methylethyl ethanoate, 2-pentanone, 2-hexanone, and hexafluoroethane were studied in a static apparatus in which the critical temperature, critical pressure, and critical volume were determined. Propene was studied in a flow apparatus in which the critical temperature and critical pressure were measured. 2-Heptanone was studied in both apparatus because of its instability at the critical point.

Experimental Section

Static Apparatus. Critical properties by the static method were measured in the apparatus shown schematically in Figure 1. The critical point cell was constructed of stainless steel with an internal volume of 100 cm^3. Glass windows were attached to the front and back of the cell to permit full visibility of the cell contents. The cell was mounted on a motorized rocking mechanism which continually moved the cell through an arc from approximately 60° above horizontal to 60° below horizontal at a rate of about once every 2 s. Rocking promoted thermal and phase equilibrium. The rocker arm could be quickly disconnected to allow the cell to be placed in a vertical position to allow observation of the cell contents and meniscus. The cell was contained in a constant-temperature forced convection oven which was controlled to within about ±0.2 K of the set point. The oven was equipped with windows on both the front and back, with back lighting to facilitate observation of the cell contents. A hand-operated syringe pump was used to pump material into and out of the cell and to control the level of the liquid phase in the cell. Temperature and pressure measurement equipment was connected to the cell through the oven wall.

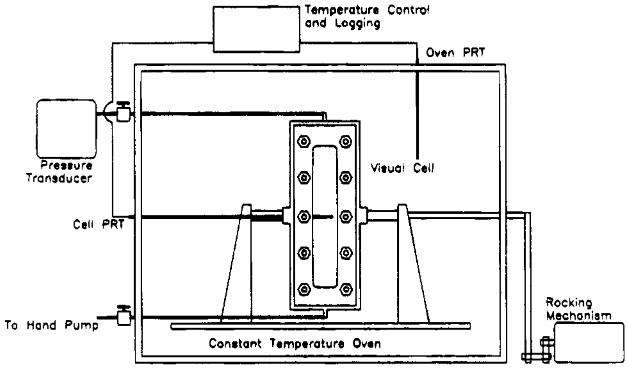

Figure 1. Static critical point apparatus.

The compounds used for the measurements were analyzed by gas−liquid chromatography to check for impurities. Most of the chemicals were dried overnight using 4 Å molecular sieves. Water analyses on the dried samples were performed by Karl Fischer titration. After the samples were dried, they were filtered and transferred to the syringe pump. No air was permitted to contact the compounds during the filtering and transferring process. The pump contents were then further degassed by evacuating the space above the liquid in the partially-filled pump.

To initiate a critical point determination, the cell was heated to near the critical temperature, and the material was pumped into the cell. The temperature of the oven was adjusted to reach the critical temperature. The amount of material in the cell was adjusted by the syringe pump so that the vapor and liquid volumes were equal as the critical point was approached. The midvolume point in the cell was calculated from the dimensions of the cell. A typical run consisted of approximately six observations of the critical temperature and pressure made during a 1 h period. The cell temperature, while passing through the critical point, changed at a rate of approximately 0.05 K·min^{-1}. The weight of material in the cell was then measured by removing the material into a cooled, weighed receiver. The receiver was weighed with an accuracy of ±0.002 g. A correction to the weight of material in the cell was made for the small amount of vapor remaining in the cell. The volume of the cell at room temperature and over the range of pressures encountered in these measurements was determined experimentally by filling from a volumetric pump. The volume at higher temperatures was calculated from the thermal coefficient of expansion of the alloy used to construct the cell.

Two runs were made on the unstable compounds. The first run was used to obtain a rough determination of the critical temperature, so that the cell could be heated to very near the critical temperature before the second run. This

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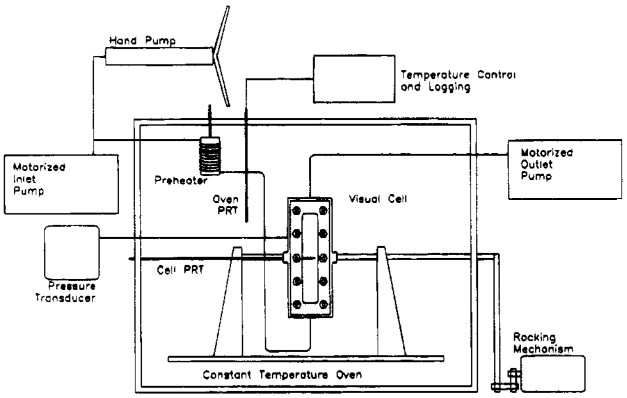

Figure 2. Flow critical point apparatus.

minimized the residence time for the second run prior to a critical point observation.

The cell temperature was measured using a platinum resistance thermometer (PRT). This thermometer was inserted into a thermowell in the cell. After each run, the cell PRT was compared with a NIST-calibrated standard platinum resistance thermometer. Temperatures were measured with an accuracy of ±0.05 K using ITS-90. The pressures were measured using a pressure transducer. The transducer has a NIST traceable calibration and was also compared to a second identical transducer after the measurements. Pressures were measured with an accuracy of ±0.7 kPa.

Flow Apparatus. A diagram of the flow apparatus is shown in Figure 2. This apparatus consists of a smaller version of the visual cell used for the static measurements connected to two motorized syringe pumps in addition to the hand-operated syringe pump. The visual cell was constructed of stainless steel and had an internal volume of 16 cm^3. Each motorized pump had a capacity of 1 L. To begin a measurement, the inlet pump was evacuated. The test fluid was dried by distilling off a small amount of material under vacuum. The purity of each compound was then checked by gas chromatography and Karl Fisher titration. The fluid was then charged to the pump and degassed in the pump by evacuating the space above the liquid in the partially-filled pump.

Meanwhile, the oven and visual cell were heated to the estimated critical temperature. The hand pump was also filled with the test fluid. The inlet pump was then activated and began pumping material through a heating coil in the oven. The heating coil was constructed of 6 m of stainless steel tubing with an inside diameter of 0.76 mm which was wrapped around a copper rod. The copper rod was heated by a cartridge-style heater inserted axially through the rod. The temperature of the copper rod was measured by a platinum resistance thermometer and controlled to the same temperature as the fluid in the visual cell.

The heated material passed through the flow cell. The exit of the flow cell was connected to the outlet pump. The outlet pump was pumped in reverse at the same rate as the inlet pump. The liquid level in the cell was adjusted by the hand pump. The visual cell was rocked to reduce thermal gradients in the cell. The material entered the bottom of the visual cell and exited through the top. The cell was rocked by the mechanism used for the larger static cell.

Approximately equal volumes of vapor and liquid were withdrawn from the cell as it rocked, thus removing degradation products from both phases in the visual cell.

The critical point of the material was visually observed at three or four flow rates by heating or cooling the oven and preheater slowly until the critical point was achieved. Care was taken to adjust the level of the liquid in the cell to give approximately equal volumes of liquid and vapor just prior to reaching the critical point. The critical temperature was measured by a PRT inserted into a thermowell in the visual cell with an accuracy of ±0.05 K. The thermowell was positioned so that the sensing portion of the PRT was surrounded by the liquid flowing through the cell. The critical pressure was measured by a pressure

Table 1. Results of Critical Point Measurements

compound	source	T_c/K	P_c/MPa	V_c/(L·mol^{-1})	Z_c
1,1-dimethylpropyl methyl ether (TAME)	Wiltec, static	536.20	3.191	0.377	0.270
1,1-dimethylethyl ethyl ether (ETBE)	Wiltec, static	509.40	2.934	0.394	0.273
ethylbenzene	Wiltec, static	617.26	3.616	0.372	0.262
	2	617.20	3.606	0.374	0.263
	7	617.15	3.609	0.374	0.263
1-methylethylbenzene	Wiltec, static	631.23	3.217	0.422	0.258
	2	631.10	3.209	0.427	0.261
	7	631.0	3.209		
1-methylethyl ethanoate	Wiltec, static	530.16	3.283	0.343	0.256
	4	530.92	3.519	0.345	0.275
2-pentanone	Wiltec, static	561.19	3.672	0.321	0.253
	1	561.1		0.301	
2-hexanone	Wiltec, static	587.61	3.287	0.378	0.254
	1	587.0			
	5	586.6		0.375	
2-heptanone	Wiltec, flow	611.4	2.940		
	Wiltec, static	611.1	2.992	0.434	0.255
	1	611.5			
	5	611.4		0.436	
toluene	Wiltec, static	591.90	4.111	0.318	0.266
	2	591.79	4.109	0.316	0.264
	7	591.75	4.108	0.316	0.263
hexafluoroethane	Wiltec, static	293.03	3.043	0.225	0.281
	2	292.80	2.979	0.224	0.274
	6	293.04	3.042	0.222	0.277
propene	Wiltec-Flow	365.16	4.594		
	2	364.76	4.613		
	3	365.57	4.665		

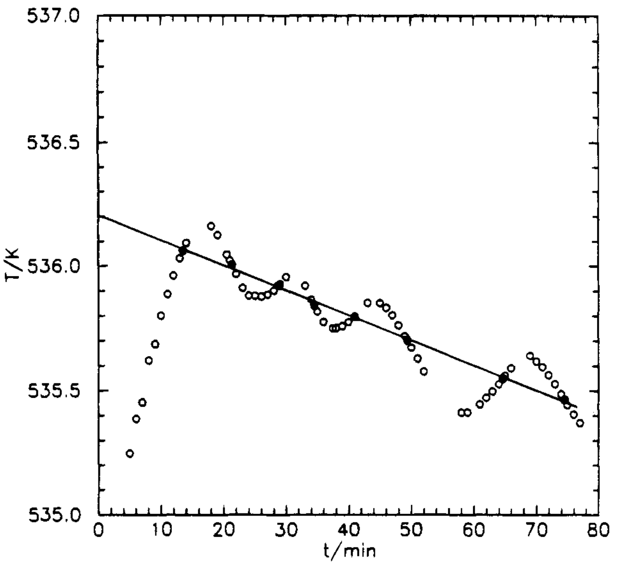

Figure 3. Critical temperature of (1,1-dimethylpropyl methyl ether versus time: ○, temperature as a function of time; ●, observed critical temperature; —, linear fit to observed critical temperatures.

transducer with an accuracy of ±0.7 kPa. The cell PRT was compared with a standard PRT immediately after each run.

The flow rates used for these measurements gave average residence times for the material in the oven of approximately 0.4–8 min. Temperature gradients in the visual cell were no more than ±0.1 K even at the highest flow rates due to the efficient design of the preheater. Temperature gradients were measured by inverting the cell so that the incoming liquid stream impinged upon the thermowell. The temperature of the incoming fluid stream was then compared with the temperature of the fluid in the cell as it was being rocked.

Results and Discussion

The results of the critical property measurements are given in Table 1. Listed in the table are the critical temperatures, critical pressures, and critical molar volumes. The critical compressibility factor has also been calculated from the measured critical temperature, pressure, and volume. Corresponding values from the literature are also given in the table where available. Some literature values are from individual measurements while others are from critical evaluations of the available literature.

Toluene, ethylbenzene, (1-methylethylbenzene, 2-pentanone, hexafluoroethane, and propene were stable at their critical points. The critical temperatures and critical pressures reported for these compounds are an average of the measured values. The critical volume was measured once at the end of the run. The measured critical temperatures are estimated to be accurate to ±0.05 K, the critical pressures are estimated to be accurate to ±5 kPa, and the critical volumes are estimated to be accurate to ±0.001 L·mol^{-1}.

The remaining five compounds showed a slow but significant change in the observed critical pressure and temperature as a function of time. Measurements were taken over a period of 60–90 min, and the reported critical temperature and pressure were determined by extrapolating back to zero residence time in the cell. An example of this is given in Figures 3 and 4, which plot the critical temperature and pressure of TAME as a function of time.

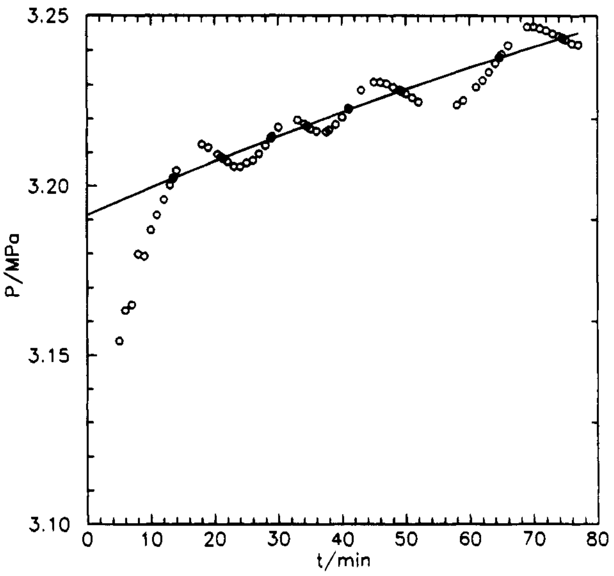

Figure 4. Critical pressure of 1,1-dimethylpropyl methyl ether versus time: ○, pressure as a function of time; ●, observed critical pressure; —, quadratic fit to observed critical pressures.

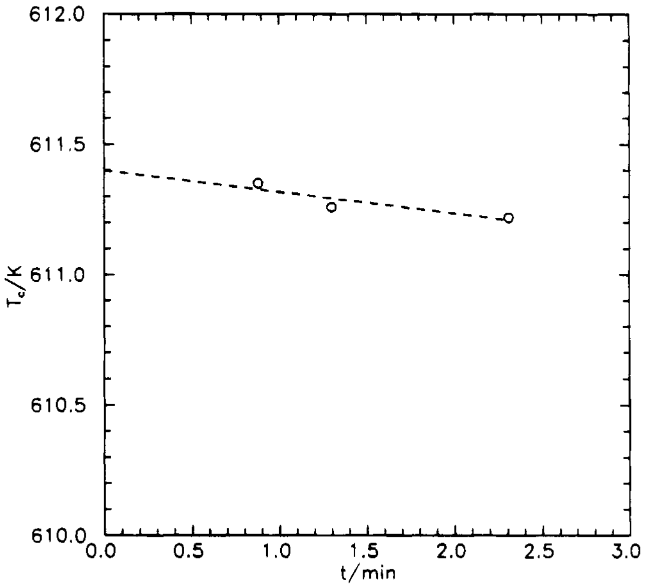

Figure 5. Critical temperature of 2-heptanone versus residence time: ○, observed critical temperature; —, linear fit to observed critical temperatures.

The critical properties of this compound changed quite linearly with time, and the critical properties at zero residence time can be extrapolated reliably. This behavior was typical of the other compounds. Critical temperatures for these five compounds have an uncertainty of ±0.2 K, and critical pressures have an uncertainty of ±40 kPa. Critical volumes have an uncertainty of ±0.001 L·mol^{-1}.

2-Heptanone was the most reactive compound studied. To check the results of the measurements in the static apparatus, the critical properties of 2-heptanone were investigated in the flow apparatus. The critical temperature and pressure were measured at three residence times and extrapolated to zero residence time. The observed critical temperature versus residence time is shown in Figure 5, and the observed critical pressure versus residence time is shown in Figure 6. The reliability of the extrapolated critical properties is primarily a function of the linearity of the measured properties as a function of residence time. For this compound, the critical temperature by the flow method is estimated to be accurate to ±0.2

Table 2. Purity of Materials Used in Critical Point Measurements

	analyzed purity/(mass %)			
compound	Wiltec	supplier	[water]/(mass %)	supplier
1,1-dimethylpropyl methyl ether	99.98	*a*	0.0090	Aldrich
1,1-dimethylethyl ethyl ether	99.4	*a*	0.0073	Phillips
ethylbenzene	99.9	99.9	0.0033	Aldrich
1-methylethylbenzene	99.9	99.9	0.0060	Aldrich
1-methylethyl ethanoate	99.97		*b*	Kodak
2-pentanone	99.9+	*a*	*b*	Aldrich
2-hexanone	99.66	99.4	0.04	Aldrich
2-heptanone	99.2	99.1	0.05	Aldrich
toluene	99.99		0.0010	Aldrich
hexafluoroethane	99.9			Du Pont
propene	99.5			Matheson

[a] Redistilled by Wiltec after being received from the supplier. [b] Dried using 4 Å molecular sieves. Typical water levels after drying are less than 0.05 mass %.

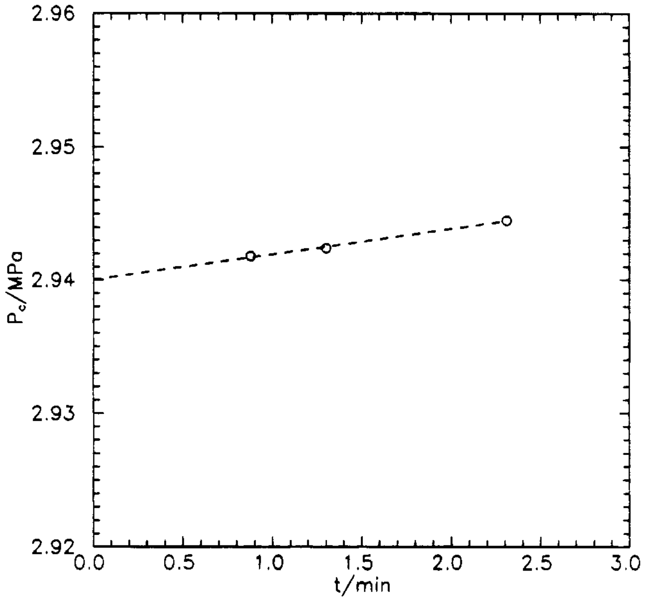

Figure 6. Critical pressure of 2-heptanone versus residence time: ○, observed critical pressure; —, linear fit to observed critical pressures.

K. The critical pressure is estimated to be accurate to ±10 kPa. The critical temperature by the flow method was 0.3 K higher than by the static method, and the critical pressure by the flow method was 52 kPa lower than by the static method. The critical temperature measured by the flow method is in better agreement with those of other researchers than the value obtained by the static method. The lower critical pressure measured in the flow apparatus is consistent with the observation that the critical pressure of 2-heptanone increases with time due to thermal decomposition. No value for the critical pressure of 2-heptanone could be found in the literature with which to compare these results.

The critical point of propene was investigated in the flow apparatus. Data at three flow rates were obtained. Static results were also obtained by stopping both pumps. The value reported in the table is an average of both static and dynamic data. There was no statistical difference between the values measured by the flow method or by the static method. These data have the same accuracy as reported for the other stable compounds.

Table 2 reports measured purities and water content for the compounds studied in this program. This table also gives the supplier for each compound.

Conclusion

Accurate critical properties have been reported for 11 compounds. Results by the static method for stable compounds are in good agreement with high-quality data in the literature. The flow method appears to give the same result as the static method for stable compounds and improves the reliability of critical temperatures and pressures obtained for unstable compounds. Because of the small volume of the flow apparatus, critical volume measurements appear to be unreliable by the flow method. To date, the flow method has been used to make measurements on 14 additional compounds with good results, most of which are significantly less stable than those measured in this work. These additional data will be ready for publication in 1996.

Acknowledgment

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