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Critical Point and Vapor Pressure Measurements at High Temperatures by Means of a New Apparatus with Ultralow Residence Times

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A new flow method has been employed to obtain critical point and vapor pressure data at high temperatures for four compounds: squalane, toluene, ethylbenzene, and styrene. This new flow method allows the determination of reliable critical points and vapor pressures for thermally unstable or otherwise reactive compounds. The critical point is inferred from other measurements in the critical region. The measurement accuracy is less than that obtained by more conventional methods, but this method has been used where conventional methods fail.

Introduction

A new flow method has been developed at Wiltec Research Company for critical point and vapor pressure measurements which involves the use of ultralow residence times. It will be of considerable interest in the following areas: (1) critical temperatures and pressures of compounds that decompose using existing methods; (2) vapor pressures of compounds that decompose using existing methods; (3) boiling points of compounds useful as the basis for critical point estimation.

The method is capable of residence times as low as 0.1 s for total heat-up time from ambient temperature. The residence time within 20 K of the measurement temperature is about 0.02 s. This new technique appears to extend our present range of measurement capability by about 100 K. Thus, for paraffin hydrocarbons, this extends the measurement range to about C30 for the critical point and to about C40 for the boiling point. In some cases it may be possible to measure vapor pressures and the boiling point where thermal decomposition prevents direct measurement of the critical point. In these cases either the vapor pressures can be extrapolated to obtain a critical temperature based on an estimated critical pressure or the boiling point can be used as a basis for estimating the critical point.

Previous critical point measurements in Wiltec's laboratory have been made either in a static apparatus or by an earlier flow method (Wilson et al., 1995). Measurements in the static apparatus involved residence times of about 30 min, and residence times in the flow apparatus were about 30 s. Another flow method (Rosenthal and Teja, 1989) using a smaller cell appears to have residence times of about 10 s. Each of these methods could be used for vapor pressure measurements. Another method developed by Nikitin and co-workers (Nikitin et al., 1993) involves the transient heating of a hot wire where residence times of 0.01−1.0 ms are achieved. The transient hot wire method requires several corrections and some extrapolation to obtain the critical point temperature and pressure, and it is unsuitable for vapor pressure measurements because the method relies on superheating. The present apparatus allows the measurement of both vapor pressures and the critical point at very low residence times. Because the method is a flow method, it would be difficult to measure critical density, so only the critical temperature (T_c) and critical pressure (P_c) are determined. Fortunately, these are the two principal critical properties of interest in process simulation calculations. It is likely this flow method can be further developed for the study of heat capacities and perhaps other properties of both liquids and gases at high temperatures.

Demonstration measurements on squalane, a C30 paraffin, have been made. In addition, three other compounds have been studied: toluene, ethylbenzene, and styrene. Measurements on toluene and ethylbenzene have been made to test the measurement method, while the results on the other two compounds represent new data.

Apparatus

The need for a short residence time at high temperature almost dictates a configuration with a very short time constant. Any static method probably suffers in that very small samples would be required and the heat capacity of the heater and sample container would interfere with rapid heat-up. A flow method where the sample is continuously displaced at steady-state conditions would only require heat to be supplied to the test stream without the need for additional heat. Thus, a flow method seems a logical choice. Unfortunately, this means that an indirect method must be used from which the critical point must be inferred. The property we have selected is that a pure compound boils isothermally when the pressure is held constant. Thus, the temperature of a liquid flowing in a small line in a temperature bath will rise smoothly as the bath temperature is raised until the boiling point is reached. At this point a transition occurs and the temperature in the line remains nearly stationary as the temperature of the bath goes higher. This can easily be seen from a scan of the temperature of the fluid in the line versus the bath temperature (see Figure 1 for examples). The advantage of the flow system is that it is not necessary to heat the bath rapidly but only that the residence time of the fluid

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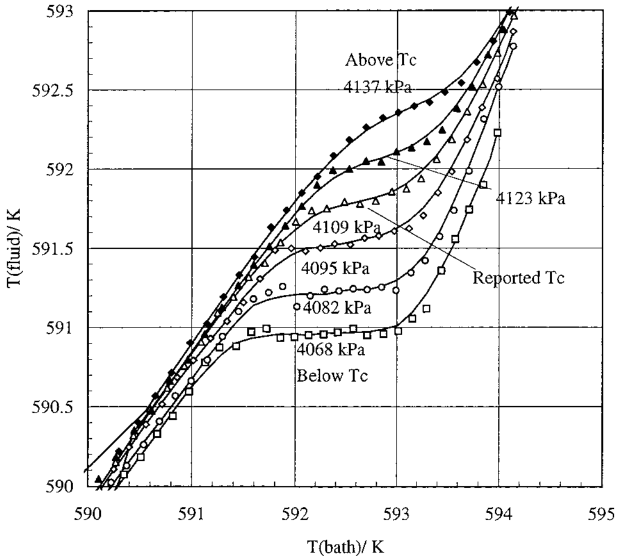

Figure 1. Temperature scans for toluene in the critical region.

in the line is short. Thus, sufficient time can be allowed to obtain a good temperature scan.

A short residence time and a fast heat-up rate can be achieved by using capillary tubing. We used 0.159 cm o.d. stainless steel tubing with an i.d. of about 0.076 cm. The capillary we used was about 38 cm long. A 0.051 cm o.d. thermocouple was inserted from the inlet end of the capillary to near the exit end of the capillary. With this configuration, the heat-up time is simply the time it takes to get heat through the capillary wall and into the fluid. Seemingly, this would be almost instantaneous, but in actuality, a fraction of a second is required. A fluid flow rate is chosen such that an element of fluid travels the distance of the length of the capillary tubing during the heat-up time. Thus, the temperature of the line reaches a steady-state condition and transferred heat only heats the sample which is continuously displaced at very low contact time.

To determine the critical point, several temperature scans must be made in the vicinity of the critical point (see Figure 1). Below the critical point, the temperature scan will show a flat, horizontal region indicative of isothermal boiling. The temperature corresponding to the run pressure can then be read off the vertical axis. Above the critical point, the transition region is no longer flat and horizontal. The critical point is inferred by the temperature and pressure where isothermal boiling is no longer observed. As can be seen from Figure 1, assigning the critical point can be somewhat subjective. For example, one could argue that the critical point is at 591.5 K and 4095 kPa, differences of 0.3 K and 14 kPa. Interpreting the temperature scans is the major source of error and can be minimized by taking several temperature scans at small intervals, as we have done here.

There are several effects that appear to blur the transition during a temperature scan. First, fluctuations in flow rate tend to smooth out the front and back of the transition to give a rounded effect. Second, impurities, including thermal degradation products, interfere with a sharp transition. These must therefore be minimized to obtain a good transition. The fast heat-up method minimizes impurities due to decomposition which would otherwise interfere with the actual critical point measurement. The flow method adopted here is probably no more subject to this effect than previous methods with the advantage that the effect can be minimized at fast heat-up times. A blurred transition can also be used as a good clue that decomposition is occurring. Finally, at low pressures, significant superheating occurs before the onset of boiling. This is manifested as a spike on the front end of the transition region. Once the fluid begins to boil, the temperature drops abruptly to the temperature corresponding to the run pressure and a good vapor pressure can be obtained. In a few cases near atmospheric pressure, a good vapor pressure could not be obtained because the spike interfered with a flat transition. Superheating was not observed near the critical pressure.

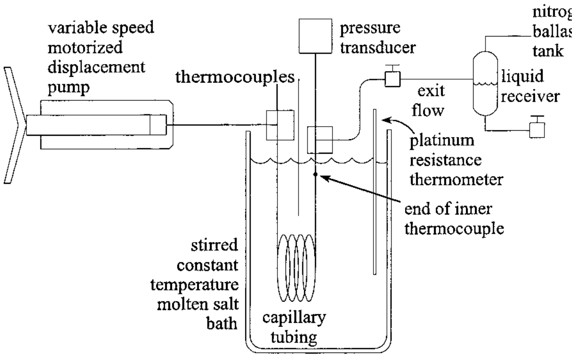

Figure 2. Schematic of flow apparatus.

A schematic drawing of the flow apparatus is shown in Figure 2. It consists of a 1000 cm^3 constant rate motorized pump, a 38 cm long capillary tube submerged in a molten salt bath, two thermocouples, a calibrated pressure transducer, a 1000 cm^3 receiving cylinder, and a 49 L ballast tank. The ballast tank is filled with nitrogen to the desired run pressure, and this pressure is regulated by a computer throughout the run. The pure compound to be tested is charged to a 1000 cm^3 constant rate motorized pump from which it is pumped continuously through a capillary line submerged in a molten salt bath. The fluid rapidly heats as it flows through the capillary to the exit end. The temperature of the fluid is measured about 2.5 cm before the exit tee. The temperature of the fluid is determined by the bath temperature as measured by a platinum resistance thermometer and the temperature difference between the two thermocouples. The pressure is measured at the exit tee. A more detailed schematic of the exit end of the capillary is given in Figure 3. The temperature and pressure data are collected by a computer logger as the salt bath is heated. Heating of the salt bath is continued as the system is held at constant pressure until the temperature is beyond the flat region corresponding to vaporization of the fluid.

Accuracy and Applicability

By the flow method outlined here, the critical point must be inferred from other measurements in the critical region. Thus, it should be considered as a supplementary method to be used where more conventional methods fail. Nevertheless, the results given here suggest that it can be reliably used considerably beyond the range of direct methods. Temperature and pressure gauges were calibrated accurately to within ±0.1 K and 0.001 MPa. The major error is in the interpretation of the temperature scans to infer the critical point. Typically, these errors appear to be about ±1.0 K in T_c and about ±2% in P_c. The vapor pressure measurements are estimated to be accurate to within ±2%. These uncertainties might be considered to be large by conventional methods, but conventional

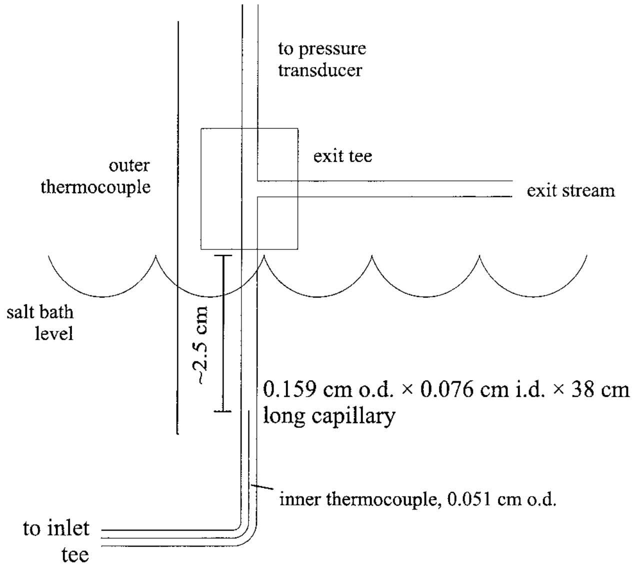

Figure 3. Detail of exit tee.

Table 1. Results of Critical Point Measurements

	T_c/K			P_c/MPa		
compound	meas	previous	est[a]	meas	previous	est[a]
squalane	795.9		882.5	0.59		0.83
toluene	591.8	591.90[b]	598.4	4.11	4.111[b]	4.13
		591.79[c]			4.109[c]	
		591.75[d]			4.108[d]	
ethylbenzene	618.0	617.26[b]	623.3	3.62	3.616[b]	3.66
		617.20[c]			3.606[c]	
		617.15[d]			3.609[d]	
styrene	635.2		644.1	3.87		3.86

[a] Estimated by the method of Joback (1984). [b] Wilson et al., 1995. [c] Daubert et al., 1995. [d] Tsonopoulos and Ambrose, 1995.

methods fail where these have not, and these accuracies are probably sufficient for validation of various estimation methods at high-temperature conditions or conditions where compounds are otherwise reactive.

Results

Table 1 presents the measured critical point temperatures and pressures for the four compounds included in this study. Where available, values are compared with values from the literature. Measurements on toluene and ethylbenzene show good agreement with earlier work, demonstrating that the method can be used to reliably measure T_c and P_c. Measurements on squalane demonstrate the applicability of the method far beyond previous measurement capabilities. Results in Table 1 for styrene also demonstrate that the method can be used where chemical instability exists or where polymerization reactions occur. There may be a host of compounds which are in either of these categories.

Table 1 also lists the estimated critical properties for these four compounds. These estimates were made using Joback's group contribution method (Joback, 1984). The predicted T_c of squalane in Table 1 is based on the boiling point reported in Daubert et al. (1995). A lower boiling point measured as part of the current project yields a predicted value of 851.3 K, which is closer to the measured value.

Tables 2−5 present vapor pressure data on the four compounds included in this study. These tables list the measured temperature and the measured and correlated pressures. The Riedel equation (Reid et al., 1977) was used to correlate the data in this study and is given below:

Table 2. Vapor Pressure of Squalane by the Low-Contact-Time Flow Method Fitted to the Riedel Equation[a]

	P/kPa				P/kPa		
T/K	meas	calc	% dev	T/K	meas	calc	% dev
628.8	22.6[b]	23.2	2.67	772.8	394[b]	407	3.39
658.9	47.8[b]	47.8	0.00	784.3	490[b]	489	−0.23
709.7	142[b]	136	−4.19	787.8	509[b]	517	1.65
712.1	145[b]	142	−1.67	790.5	536[b]	539	0.68
732.0	208[b]	205	−1.63	795.9	590[b]	587	−1.04
749.7	281[b]	278	−0.91	521.2	0.67[c]	0.67	0.06
769.2	381[b]	384	0.98	536.2	1.33[c]	1.23	−7.95

[a] Riedel parameters fitting only P_c and α: $a = 151.96$; $b = -20\,738.01$; $c = -18.0037$; $d = 2.847\,44 \times 10^{-18}$; $T_c = 795.9$ K; fitted $P_c = 587.2$ kPa; $\alpha = 12.394\,98$. [b] This work. [c] Budavari et al., 1996 (not fitted).

Table 3. Vapor Pressure of Toluene by the Low-Contact-Time Flow Method Fitted to the Riedel Equation[a]

	P/kPa				P/kPa		
T/K	meas	calc	% dev	T/K	meas	calc	% dev
586.3	3900[b]	3870	−0.73	591.6	4140[b]	4130	−0.27
586.4	3900[b]	3880	−0.62	590.6	4070[b]	4080	0.29
589.3	4050[b]	4020	−0.92	590.9	4070[b]	4090	0.64
589.5	4050[b]	4030	−0.70	590.4	4070[b]	4070	0.07
590.4	4100[b]	4070	−0.79	590.7	4070[b]	4080	0.43
590.5	4100[b]	4070	−0.67	590.7	4070[b]	4080	0.43
590.8	4140[b]	4090	−1.13	591.0	4070[b]	4100	0.77
591.7	4140[b]	4130	−0.05	591.3	4130[b]	4110	−0.48
590.4	4070[b]	4070	0.07	591.6	4140[b]	4130	−0.17
590.4	4070[b]	4070	0.05	590.7	4070[b]	4080	0.41
591.1	4100[b]	4100	0.05	590.9	4070[b]	4090	0.65
591.2	4100[b]	4110	0.17	590.4	4070[b]	4070	0.04
590.9	4100[b]	4090	−0.19	590.6	4070[b]	4080	0.31
591.1	4100[b]	4100	0.05	591.0	4100[b]	4100	0.10
591.8	4140[b]	4140	0.04	591.3	4100[b]	4110	0.46
589.0	4020[b]	4000	−0.58	591.5	4120[b]	4120	0.01
589.1	4020[b]	4010	−0.42	591.8	4110[b]	4140	0.77
589.9	4070[b]	4050	−0.68	325.0	13.3[c]	13.10	−1.21
590.0	4070[b]	4050	−0.53	350.0	34.8[c]	34.57	−0.61
591.2	4140[b]	4110	−0.63	375.0	78.5[c]	78.59	0.08
591.8	4130[b]	4140	0.10	400.0	157.6[c]	158.63	0.64
591.2	4070[b]	4060	−0.29	425.0	287.9[c]	290.98	1.05
590.3	4070[b]	4070	−0.15	450.0	488.0[c]	494.01	1.22
590.8	4110[b]	4090	−0.39	475.0	778.4[c]	787.76	1.19
590.9	4110[b]	4090	−0.27	500.0	1182.4[c]	1194.15	0.98
591.4	4140[b]	4120	−0.51	525.0	1725.1[c]	1738.34	0.77

[a] Riedel parameters fitting only P_c and α: $a = 47.922\,43$; $b = -5969.427$; $c = -4.666\,473$; $d = 6.522\,369 \times 10^{-18}$; $T_c = 591.80$ K; fitted $P_c = 4141.6$ kPa; $\alpha = 7.10158$. [b] This work. [c] Daubert et al., 1995 (fitted).

$$\ln(P/\text{kPa}) = a + \frac{b}{(T/\text{K})} + c\ln(T/\text{K}) + d(T/\text{K})^6 \qquad (1)$$

where a, b, c, and d are parameters related to P_c and a parameter α by the following relationships:

$$a = -35Q - c\ln(T_c) + \ln(P_c) \qquad b = 36QT_c$$

$$c = 42Q + \alpha \qquad d = -\frac{Q}{T_c^{\,6}} \quad \text{where}$$

$$Q = 0.0838(3.758 - \alpha) \qquad (2)$$

The correlations listed in the tables were obtained by varying only P_c and α. These values, as well as the resulting

Table 4. Vapor Pressure of Ethylbenzene by the Low-Contact-Time-Flow Method Fitted to the Riedel Equation[a]

	P/kPa				P/kPa		
T/K	meas	calc	% dev	T/K	meas	calc	% dev
492.7	618[b]	620	0.36	618.0	3620[b]	3590	−0.72
573.1	2070[b]	2070	−0.28	325.0	5.13[c]	5.12	−0.12
573.0	2070[b]	2060	−0.44	350.0	14.88[c]	14.82	−0.37
595.6	2750[b]	2750	−0.14	375.0	36.48[c]	36.41	−0.19
596.5	2750[b]	2780	0.99	400.0	78.39[c]	78.46	0.09
613.5	3430[b]	3410	−0.62	425.0	151.62[c]	152.14	0.35
614.0	3430[b]	3430	−0.03	450.0	269.45[c]	270.74	0.48
618.0	3620[b]	3590	−0.68	475.0	447.40[c]	449.19	0.40

[a] Riedel parameters fitting only P_c and α: $a = 50.961\,22$; $b = -6524.055$; $c = -5.058\,866$; $d = 5.263\,757 \times 10^{-18}$; $T_c = 618.00$ K; fitted $P_c = 3593.9$ kPa; $\alpha = 7.25731$. [b] This work. [c] Daubert et al., 1995 (fitted).

Table 5. Vapor Pressure of Styrene by the Low-Contact-Time Flow Method Fitted to the Riedel Equation[a]

	P/kPa				P/kPa		
T/K	meas	calc	% dev	T/K	meas	calc	% dev
473.3	360[b]	360	−0.07	610.7	2890[b]	2900	0.13
474.3	361[b]	367	1.72	629.0	3610[b]	3590	−0.43
489.2	489[b]	488	−0.15	630.3	3610[b]	3650	1.09
490.4	491[b]	499	1.64	628.7	3610[b]	3580	−0.70
510.0	709[b]	705	−0.60	629.6	3610[b]	3620	0.32
511.4	709[b]	721	1.66	628.2	3610[b]	3560	−1.44
532.0	1010[b]	1000	−0.29	628.9	3610[b]	3590	−0.64
532.6	1010[b]	1010	0.57	634.7	3870[b]	3840	−0.87
551.0	1340[b]	1330	−0.38	635.2	3870[b]	3860	−0.19
551.0	1340[b]	1330	−0.38	325.0	3.52[c]	3.52	0.02
570.3	1750[b]	1740	−0.61	350.0	10.76[c]	10.66	−0.93
570.9	1750[b]	1750	0.24	375.0	27.39[c]	27.18	−0.79
590.6	2280[b]	2260	−0.89	400.0	60.51[c]	60.50	−0.02
591.5	2280[b]	2290	0.28	425.0	119.49[c]	120.62	0.95
610.0	2890[b]	2870	−0.74				

[a] Riedel parameters fitting only P_c and α: $a = 51.558\,39$; $b = -6744.184$; $c = -5.109\,557$; $d = 4.490\,074 \times 10^{-18}$; $T_c = 635.20$ K; Fitted $P_c = 3862.7$ kPa; $\alpha = 7.277\,43$. [b] This work. [c] Daubert et al., 1995 (fitted).

Table 6. Source and Purity of Materials Used in These Measurements

		analyzed purity/mass %			
compound	CASRN	this work	supplier	water mass %	supplier
toluene	108-88-3	99.8%	99.8%	0.02%	Aldrich
ethyl benzene	100-41-4	99.9%	99.%	0.08%	Aldrich
squalane	111-01-3	99.9%	99.%	0.01%	Aldrich
styrene	100-42-5	99.9%[1]	99.%	0.03%	Aldrich

values for a, b, c, and d are given at the bottom of each table. Literature references labeled as “not fitted” were not used in correlating the data. Those labeled as “fitted” were used in the correlation and demonstrate consistency between these data and data previously measured. The values of P_c listed in these tables differ from the values in Table 1 because P_c was used as a parameter to fit the vapor pressure data.

Table 6 summarizes the source and purity of the compounds used for these measurements. All of the materials were purchased from Aldrich Chemical Co. and had purities of 99% or higher. Karl Fischer titrations on the compounds show very low water content.

Conclusion

A new flow method has been employed to obtain critical point and vapor pressure measurements at high temperatures for four compounds. This new flow method allows the determination of reliable critical points and vapor pressures for thermally unstable or otherwise reactive compounds. The critical point is inferred from other measurements in the critical region. Measurement accuracy is less than that obtained by more conventional methods, but this method can be used where conventional methods fail.

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