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Critical Point and Vapor Pressure Measurements for Four Compounds by a Low Residence Time Flow Method[†]

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Critical temperature, critical pressure, and vapor pressure measurements have been performed on three compounds by a flow method with ultralow residence times. These compounds are as follows: 1,6-hexanediol, 1,3-benzenediol, and piperazine. Accurate vapor pressure data are also included for 1,2-benzenediol, but this compound proved too unstable to directly determine the critical constants using this apparatus.

Introduction

This work is part of an ongoing investigation of the critical properties for compounds selected for industrial interest in 2001 by sponsors of Project 851 of the Design Institute for Physical Properties (DIPPR) of the American Institute of Chemical Engineers (AIChE). This paper reports experimental measurements of the critical properties and vapor pressures for three compounds studied in a flow apparatus with ultralow residence times. These three compounds are 1,6-hexanediol (Chemical Abstracts Service Registry Number or CASRN 629-11-8), 1,3-benzenediol (CASRN 108-46-3), and piperazine (CASRN 110-85-0). Accurate vapor pressures are also reported for 1,2-benzenediol (CASRN 120-80-9), but this compound proved too unstable to determine the critical constants using this apparatus.

Experimental Section

The flow apparatus and procedures used for these measurements are modified from those previously used.[1] In brief, the fluid to be tested flows at constant pressure through a capillary tube containing a thermocouple. As the temperature of the fluid increases, it goes through a phase change. Below the critical pressure, this material boils at "constant" temperature. Above the critical pressure, this change in state does not occur isothermally. This process produces temperature scans similar to the sample scans for 1,6-hexanediol shown in Figure 1. This plot shows that, below the critical pressure, the temperature scan is flatter and shows a distinct break as the fluid goes from two phases to a single vapor phase. The scans above the critical point do not show this behavior. The reported critical point is between the lowest scan above the critical point and the highest scan below the critical point. Temperatures are measured on the ITS-90. Temperature and pressure measurements have uncertainties of ± 0.1 K and ± 0.7 kPa, respectively.

Because these compounds are solids at room temperature, having melting points ranging from (315 to 382) K, the apparatus is modified to pump these materials through the capillary tubing. The compound to be tested is charged to a 500 cm^3 floating piston displacement cylinder and placed in a stirred, constant temperature bath. This bath is maintained at a temperature about 10 K above the melting point of the compound to be tested. The motorized pump is filled with diethylene glycol and connected to the upstream side of the displacement cylinder. Using the diethylene glycol to displace the test fluid, the compound to be tested is pumped through the capillary line where the measurements are made. The tubing carrying the test fluid to and from the capillary is heat traced with heater wire, and the receiver cell where the test fluid accumulates after having flowed through the apparatus is placed in the same bath as the displacement cylinder.

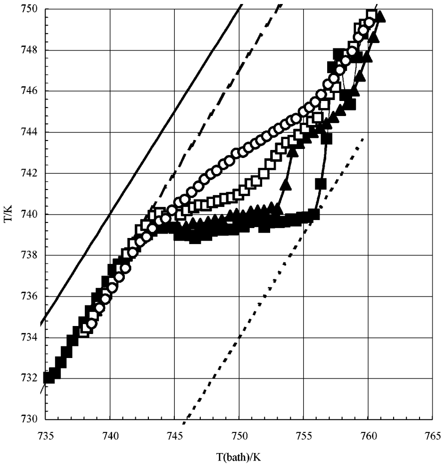

Figure 1. Sample temperature scans for 1,6-hexanediol. Temperature scans at ○, 4201 kPa; □, 4104 kPa; ▲, 4054 kPa; and ■, 4012 kPa. − −, no vaporization; - - -, full vaporization; —, $T = T$(bath).

Care was taken to purchase the compounds at high purity. Water and dissolved gases were removed by heating the material above its melting point and distilling off a small amount of material under vacuum, but no further attempts were made to purify the chemicals. Table 1 reports measured purities and water content for the compounds studied in this work. The purities were measured at Wiltec using gas chromatography. The water analyses were performed using Karl Fischer titration. These analyses were performed on the material after the distillation step. The supplier and CASRN of each chemical are also listed.

After flowing through the capillary where the vapor pressure and critical point measurements are made, the material collects in a receiving cylinder. For each of the compounds, samples were taken of the material in this receiving cylinder. These

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Table 1. Source and Purity of Materials

compound	CASRN	analyzed purity mass fraction Wiltec^a	analyzed purity mass fraction supplier	water, mass fraction	supplier
1,6-hexanediol	629-11-8	0.9997	0.987	0.0017	Aldrich
1,2-benzenediol	120-80-9	0.995	0.995	0.0004	Aldrich
1,3-benzenediol	108-46-3	0.999	0.999	0.0007	Aldrich
piperazine	110-85-0	0.999+	0.999	0.0011	Aldrich

[a] On a water-free basis.

Table 2. Results of Critical Temperature T_c and Pressure p_c Measurements

Section A: T_c and p_c Measurements on Three Compounds

compound	T_c/K measd^a	T_c/K previous	T_c/K estd^b	p_c/MPa measd^a	p_c/MPa previous	p_c/MPa estd^b
1,6-hexanediol	740.8		741	4.08		3.89
1,3-benzenediol	836		824	6.24		5.79
piperazine	656.3	661.0^c	635	5.42	5.8^c	5.39

Extrapolated T_c and p_c for 1,2-Benzenediol

compound	T_c/K result^d	T_c/K estd^b	p_c/MPa result^d	p_c/MPa estd^b
1,2-benzenediol	800	773	6.24	5.43

[a] T_c and p_c for 1,3-benzenediol have uncertainties of ± 5 K and ± 5 %, respectively. Uncertainties for the other values are ± 2 K in T_c and ± 2 % in p_c. [b] Estimated critical temperatures based on the first-order atomic contribution method of Wilson and Jasperson[2] using the boiling points measured as part of this project. Estimated critical pressures based on the estimated critical temperatures and the first-order atomic contribution method of Wilson and Jasperson.[2] [c] Steele et al.[3] report an uncertainty of 1 K in T_c. p_c is a derived parameter, and they do not report an uncertainty for this value. [d] It is estimated that p_c of 1,2-benzenediol is equal to the p_c of 1,3-benzenediol. T_c of 1,2-benzenediol is then obtained by extrapolating the vapor pressure equation given at the bottom of Table 5 to this p_c. p_c obtained in this fashion is estimated to have an uncertainty of ± 10 %, which translates into an uncertainty of ± 10 K in T_c.

Table 3. Normal Boiling Points T_b Obtained from the Reported Correlations

compound	T_b/K this work	T_b/K previous
1,6-hexanediol	525.8	525.95^a
1,2-benzenediol	519.8	518.65^b
1,3-benzenediol	554.0	549.65^b
piperazine	421.7	421.77^c

[a] Ref 4. [b] Ref 5. [c] Ref 3.

Table 4. Vapor Pressure p of 1,6-Hexanediol

T/K	p/kPa measd	p/kPa corrltd^a	dev/%	T/K	p/kPa measd	p/kPa corrltd^a	dev/%
740.4	4054	4062	0.18	480.78	25.02^b	25.06	0.14
740.0	4012	4044	0.79	474.49	19.93^b	19.95	0.09
717.6	3024	3030	0.20	469.70	16.67^b	16.67	0.02
685.1	2007	1973	−1.69	463.94	13.33^b	13.33	−0.01
637.1	1001	985	−1.57	458.37	10.67^b	10.65	−0.12
597.1	500.6	499.4	−0.23	451.48	7.999^b	7.983	−0.20
552.8	199.3	199.6	0.14	442.28	5.333^b	5.318	−0.28
523.2	93.33	94.46	1.22	436.09	4.000^b	3.990	−0.26
559.49	232.0^b	232.5	0.21	429.96	2.976^b	2.966	−0.36
552.69	198.5^b	199.1	0.30	427.76	2.666^b	2.658	−0.29
545.94	169.0^b	169.7	0.38	424.97	2.317^b	2.308	−0.39
539.24	143.3^b	143.9	0.45	422.15	2.000^b	1.996	−0.20
532.57	120.8^b	121.4	0.48	420.07	1.797^b	1.790	−0.41
525.95	101.3^b	101.8	0.49	414.97	1.367^b	1.361	−0.41
519.38	84.53^b	84.95	0.50	404.97	0.7762^b	0.7730	−0.41
512.84	70.12^b	70.44	0.45	394.97	0.4232^b	0.4215	−0.39
506.35	57.82^b	58.06	0.42	384.97	0.2204^b	0.2199	−0.21
499.90	47.38^b	47.55	0.36	374.98	0.1095^b	0.1094	−0.06
493.00	38.57^b	38.06	−1.30	364.98	0.05150^b	0.05162	0.24
487.12	31.18^b	31.25	0.24	354.98	0.02270^b	0.02299	1.28
480.79	25.02^b	25.07	0.18				

[a] $A = 172.160$, $B = -17748.3$, $C = -20.2720$, $D = 5.88971 \times 10^{-18}$. [b] Ref 4.

samples were then analyzed using gas chromatography to determine how much the compound decomposed during the measurements. All of the samples taken from the receiving cylinder exhibited purities greater than 97 %. Because the residence time before the point where the measurements were made was less than 10 % of the residence time after this point, most of the decomposition would occur after the material has exited the capillary tubing where the measurements are made. Significant deviations from the "normal" shape of a vapor pressure curve are a good indication of when significant decomposition is occurring.

Results and Discussion

Table 2, Section A, presents the measured critical point values for three of the compounds included in this study as well as estimated critical values for these compounds. The estimated critical temperatures were obtained using the boiling points reported in Table 3 and the first-order atomic contribution method of Wilson and Jasperson as presented in Poling et al.[2] The estimated critical pressures were obtained using the estimated critical temperatures and the first-order atomic contribution method of Wilson and Jasperson.[2] Where available, measured values from the literature are also given. Due to plugging of the capillary tubing, fewer temperature scans for 1,3-benzenediol were obtained in the critical region. Based on the difference between the highest scan below the critical point and the lowest scan above the critical point, the critical temperature and pressure reported in Table 2, Section A, for this compound have estimated uncertainties of ± 5 K and ± 5 %, respectively. The critical temperatures and pressures reported in Table 2, Section A, for the other compounds are estimated to have uncertainties of ± 2 K and ± 2 %, respectively. Due to the lower residence times possible with this method, these newly measured values are believed to be more reliable than the previous values shown in Table 2.

1,2-Benzenediol proved to be too unstable to directly determine the critical constants using this apparatus. Table 2, Section B, presents estimated critical point values for this compound. The critical pressure is estimated to be equal to the critical pressure obtained for 1,3-benzenediol. The reported critical temperature is then obtained by extrapolating the vapor pressure equation obtained as part of this project to this estimated critical pressure. It is estimated that the critical pressure obtained in this fashion is uncertain to within ± 10 %, which translates into an uncertainty of ±10 K in the critical temperature.

Table 3 presents the normal boiling point T_b for each of the compounds included in this study. These values were obtained using the reported correlations given at the bottom of Tables 4 through 7. Measured T_b values reported by other researchers listed in Tables 4 through 7 are also listed. Agreement is good for 1,6-hexanediol and piperazine. For the benzenediols, T_b for this work is higher than von Terres et al.[5]

Tables 4 through 7 present vapor pressure data on the four compounds included in this study. These tables list the measured temperature and the measured and correlated vapor pressures. The reported correlations of the measured data demonstrate the internal consistency of the measured data and show, where applicable, that these data agree with data previously measured

Table 5. Vapor Pressure *p* of 1,2-Benzenediol

	p/kPa				p/kPa		
T/K	measd	corrltd[a]	dev/%	T/K	measd	corrltd[a]	dev/%
754.8	3993	4010	0.42	510.95	86.66[b]	81.46	−6.00
753.5	4007	3957	−1.25	508.15	79.99[b]	75.88	−5.15
727.9	2997	3013	0.51	504.55	73.33[b]	69.16	−5.68
727.5	2993	2999	0.21	501.35	66.66[b]	63.61	−4.58
711.5	2496	2503	0.27	497.75	60.00[b]	57.80	−3.66
692.7	1995	2000	0.22	493.35	53.33[b]	51.30	−3.80
692.7	1996	2000	0.19	488.95	46.66[b]	45.42	−2.66
640.9	992.8	997.3	0.45	486.45	43.33[b]	42.34	−2.30
640.1	988.9	985.6	−0.33	484.05	40.00[c]	39.54	−1.15
621.8	742.9	745.6	0.36	477.95	33.33[c]	33.11	−0.65
597.3	499.4	497.0	−0.49	471.15	26.66[c]	27.00	1.26
595.6	487.9	482.5	−1.11	461.35	20.00[c]	19.87	−0.64
577.6	349.1	348.1	−0.28	449.35	13.33[c]	13.36	0.22
547.0	187.4	188.3	0.51	441.15	10.00[c]	10.04	0.42
535.7	147.0	146.9	−0.05	430.15	6.666[c]	6.709	0.64
511.3	81.47	82.18	0.88	412.45	3.333[c]	3.327	−0.19
518.65	101.32[b]	98.57	−2.71	391.65	1.333[c]	1.328	−0.38
514.15	93.33[b]	88.25	−5.44				

[a] $A = 62.8121$, $B = -9274.10$, $C = -5.35036$, $D = 0.718561 \times 10^{-18}$. [b] Ref 5, not used in correlation. [c] Ref 5, used in correlation.

Table 6. Vapor Pressure *p* of 1,3-Benzenediol

	p/kPa				p/kPa		
T/K	measd	corrltd[a]	dev/%	T/K	measd	corrltd[a]	dev/%
831.3	5995	5962	−0.56	530.15	60.00[b]	55.28	−7.85
813.7	4999	5034	0.71	525.15	53.33[b]	48.26	−9.50
790.6	3994	3994	0.00	521.15	46.66[b]	43.20	−7.43
728.6	1994	2000	0.28	519.15	43.33[b]	40.83	−5.77
675.9	994.4	992.1	−0.24	513.35	40.00[b]	34.57	−13.56
631.7	494.8	492.8	−0.41	510.15	33.33[b]	31.48	−5.56
582.6	192.6	193.0	0.22	503.25	26.66[b]	25.58	−4.05
546.7	84.54	84.75	0.25	494.85	20.00[c]	19.69	−1.57
549.65	101.33[b]	91.15	−10.04	483.15	13.33[c]	13.41	0.57
546.15	93.33[b]	83.60	−10.42	474.85	10.00[c]	10.07	0.67
543.15	86.66[b]	77.54	−10.52	463.45	6.666[c]	6.652	−0.21
540.15	79.99[b]	71.85	−10.18	446.15	3.333[c]	3.375	1.25
537.15	73.33[b]	66.50	−9.31	424.65	1.333[c]	1.322	−0.88
534.15	66.66[b]	61.48	−7.77				

[a] $A = 83.8719$, $B = -11768.1$, $C = -8.09389$, $D = 0.910102 \times 10^{-18}$. [b] Ref 5, not used in correlation. [c] Ref 5, used in correlation.

Table 7. Vapor Pressure *p* of Piperazine

	p/kPa				p/kPa		
T/K	measd	corrltd[a]	dev/%	T/K	measd	corrltd[a]	dev/%
655.0	5348	5333	−0.29	460.48	270.0[b]	269.9	−0.02
653.7	5243	5257	0.27	453.92	232.0[b]	231.9	−0.04
649.3	4994	5007	0.26	447.40	198.5[b]	198.4	−0.05
629.7	3997	4009	0.31	440.93	169.0[b]	169.0	−0.04
573.6	1994	1979	−0.76	434.49	143.2[b]	143.2	−0.02
528.1	992.6	998.4	0.59	428.10	120.8[b]	120.8	0.05
488.9	492.3	492.7	0.07	421.77	101.3[b]	101.5	0.15
471.6	343.6	345.1	0.43	418.00	90.98[b]	91.18	0.23
445.2	189.5	188.0	−0.83				

[a] $A = 61.6985$, $B = -7247.89$, $C = -5.46043$, $D = 3.35962 \times 10^{-18}$. [b] Ref 3.

on these compounds. The Riedel equation[2] was used to correlate the data in this study and is given below:

$$\ln(p/\text{Pa}) = A + \frac{B}{T/\text{K}} + C\ln(T/\text{K}) + D(T/\text{K})^6$$

where A, B, C, and D are parameters. The values for these parameters obtained from a least-squares regression are given at the bottom of each table. The vapor pressures measured as part of this project have an estimated uncertainty of ± 2 %. For 1,2-benzenediol and 1,3-benzenediol, some of the data reported by von Terres et al.[5] were not used in obtaining the reported correlations because they did not agree with the data measured as part of this project.

Table 8. Critical Point Values T_c and p_c of Normal Aliphatic Diols

	T_c/K		p_c/MPa	
compound	measd	estd[a]	measd	estd[a]
1,2-ethanediol	719 ± 6[b] 718 ± 9[c] 720 ± 7[d]	715	8.2 ± 0.4[b] 8.2 ± 0.3[d]	8.4
1,3-propanediol	718.2 ± 2.0[e] 722 ± 4[b]	724	6.55 ± 0.13[e] 6.3 ± 0.6[b]	6.6
1,4-butanediol	723.8 ± 2.0[e]	732	5.52 ± 0.11[e]	5.4
1,6-hexanediol	740.8 ± 2.0[f]	741	4.08 ± 0.08[f]	3.9

[a] Estimated using the first-order method of Wilson and Jasperson.[2] [b] Ref 6. [c] Ref 8. Teja and Rosenthal[10] later attempted measurements on 1,2-ethanediol and reported that they could not achieve a supercritical state up to the pressure limit of their apparatus 9 MPa and a corresponding temperature of 720 K. [d] Ref 9. [e] Ref 7. [f] This work.

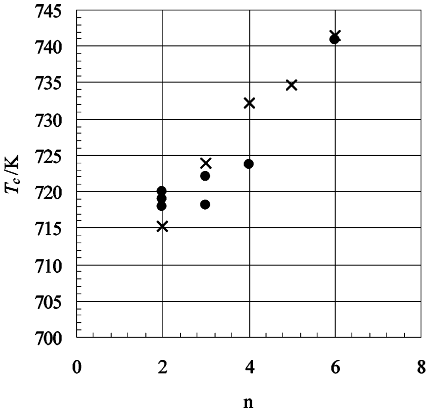

Figure 2. Critical temperature T_c of normal aliphatic diols as a function of carbon number n: ●, measured critical temperatures; ×, estimated critical temperatures.

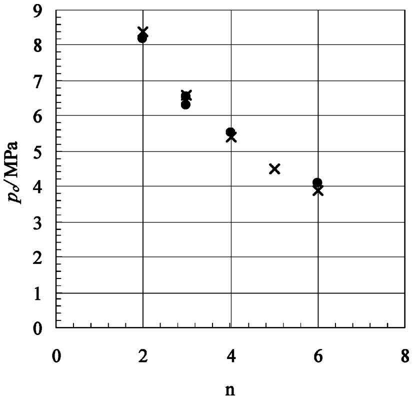

Figure 3. Critical pressure p_c of normal aliphatic diols as a function of carbon number n: ●, measured critical pressures; ×, estimated critical pressures.

Table 8 presents a summary of measured critical temperatures and pressures for normal aliphatic diols [HO-(CH$_2$)$_n$-OH] measured in this laboratory since 1995. These compounds are 1,2-ethanediol,[6] 1,3-propanediol,[6,7] 1,4-butanediol,[7] and 1,6-hexanediol (this work). A review of the literature located measured values for 1,2-ethanediol published by other researchers.[8,9] Teja and Rosenthal[10] attempted measurements on 1,2-ethanediol and reported that they could not achieve a supercritical state up to the pressure limit of their apparatus 9 MPa and a corresponding temperature of 720 K. Estimated values using the first-order method of Wilson and Jasperson[2] are also listed. Figures 2 and 3 show plots of the critical temperatures and pressures as functions of carbon number. From this analysis, semi-quantifiable trends between the measured critical point values and carbon number can be seen. The estimated critical properties show similar trends.

Conclusions

Accurate vapor pressures have been measured on four compounds of industrial significance, and reliable critical point values have been measured for three of these four compounds. The critical point values of 1,2-benzenediol were not obtained using this apparatus because this compound proved too unstable. Using the measured vapor pressure data and the data obtained for 1,3-benzenediol, reasonable estimates for the critical temperature and pressure of 1,2-benzenediol were obtained and reported. These data are useful in many engineering applications and in evaluating the applicability of current predictive techniques. They will also be useful in developing better correlations for estimating critical temperatures and pressures.

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