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

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Critical temperature, critical pressure, and vapor pressure measurements have been performed on seven compounds by a flow method with ultralow residence times. These compounds along with their Chemical Abstract Services Registry numbers are as follows: 2-phenylethanol (60-12-8), 1-*tert*-butoxy-2-propanol (57018-52-7), 2-propene-1-ol (107-18-6), 1-dodecanethiol (112-55-0), thioanisole (100-68-5), naphthalene (91-20-3), and triacontane (638-68-6). While accurate vapor pressure data are included for triacontane, this compound proved too unstable to directly determine the critical constants using this apparatus. Accurate vapor pressures, critical temperatures, and critical pressures are included for the other compounds.

Introduction

This work is part of an ongoing investigation of the critical properties for compounds selected for industrial interest in 1998 by sponsors of Project 851 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers (AIChE). This paper reports experimental measurements of the critical properties and vapor pressures for six compounds studied in a flow apparatus with ultralow residence times. These six compounds are 2 phenylethanol (CASRN 60-12-8), 1-*tert*-butoxy-2-propanol (CASRN 57018-52-7), 2-propene-1-ol (CASRN 107-18-6), 1-dodecanethiol (CASRN 112-55-0), thioanisole (CASRN 100-68-5), and naphthalene (CASRN 91-20-3). Accurate vapor pressures are also reported for triacontane (CASRN 638-68-6), but this compound proved too unstable to measure the critical constants using this apparatus.

Experimental Section

The flow apparatus and procedures used for these measurements have been described previously.[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 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 scan above the critical point does 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.

For naphthalene and triacontane, which melt above room temperature, a 700 cm^3 displacement coil charged with the solid compound was placed between the pump and the capillary tubing in the salt bath. This coil was placed in a constant-temperature bath controlled above the melting point of the compound to be tested. Vegetable oil was then charged to the pump and used to displace the test fluid. Temperatures were measured on the ITS-90. Temperature and pressure measurement devices were calibrated to within ± 0.1 K and ± 0.7 kPa, respectively.

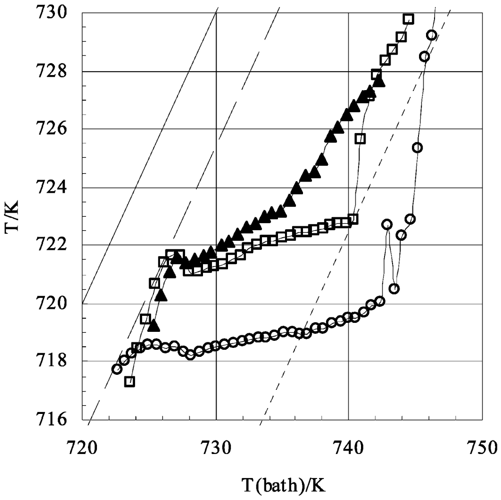

Figure 1. Sample temperature scans for 2-phenylethanol. Temperature scan at ○, 3793 kPa; □, 3966 kPa; ▲, 4013 kPa. − −, no vaporization; ---, full vaporization; −, $T = T$(bath).

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. Care was taken to purchase the compounds at high purity. 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. These analyses were performed on the material after the distillation step. The supplier and Chemical Abstract Services Registry Number (CASRN) of each chemical are also listed.

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† This contribution will be part of a special print edition containing papers reporting experimental results from the various projects of the Design Institute for Physical Properties of the American Institute of Chemical Engineers.

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Table 1. Source and Purity of Materials

		analyzed purity mass fraction			
compound	CASRN[a]	Wiltec	supplier	water, mass fraction	supplier
2-phenylethanol	60-12-8	0.999	0.999	0.0005	Aldrich
1-*t*-butoxy-2-propanol	57018-52-7	0.999	0.997	0.0011	Aldrich
2-propene-1-ol	107-18-6	0.9999	0.995	0.0006	Aldrich
1-dodecanethiol	112-55-0	0.995	0.992	0.0003	Aldrich
thioanisole	100-68-5	0.995	0.998	0.0004	Aldrich
naphthalene	91-20-3	0.999	0.999	0.0006	Aldrich
triacontane	638-68-6	0.995	0.996	0.0002	Acros

[a] CASRN, Chemical Abstracts Service Registry Number.

Table 2. Critical Temperature T_c and Pressure p_c Measurements

Section a: Results of Measurements on Six Compounds

	T_c/K			p_c/MPa		
compound	measd[a]	previous	estd[b]	measd[a]	previous	estd[b]
2-phenylethanol	723.5		726.4	3.99		3.92
1-*t*-butoxy-2-propanol	600.7		587.9	2.72		2.67
2-propene-1-ol	547.1	545.1[c]	580.6	5.64		6.75
1-dodecanethiol	733.7		737.3	1.81		1.88
thioanisole	705.9		717.6	4.05		4.11
naphthalene	750.0	748.4[d]	755.5	4.13	4.05[d]	4.04

Section b: Extrapolated for Triacontane

	T_c/K			p_c/MPa	
compound	result[e]	previous	est[b]	previous	est[b]
triacontane	842	843[f]	840.6	0.636[f]	0.66

[a] Measured values from this work have estimated uncertainties of ± 2 K in T_c and ± 2 % in p_c. [b] Estimated critical values based on the first-order atomic contribution method of Wilson and Jasperson[5] using the normal boiling points measured as part of this project. [c] Gude and Teja[6] do not report an uncertainty for this value. [d] Tsonopoulos and Ambrose[4] report an uncertainty of ± 0.5 K in T_c and ± 0.05 MPa in p_c. [e] p_c is estimated using the first-order atomic contribution method of Wilson and Jasperson[5] and the normal boiling point measured as part of this project. T_c is then obtained by extrapolating the vapor pressure equation reported in Table 9 to this p_c. p_c obtained in this fashion has an estimated uncertainty of ± 10 %, which translates into an uncertainty of ± 10 K in T_c. [f] Nikitin et al.[7] report uncertainties of ± 13 K in T_c and ± 0.025 MPa in p_c.

Table 3. Vapor Pressure *p* of 2-Phenylethanol

	p/kPa				*p*/kPa		
T/K	measd	correlated[a]	dev/%	*T*/K	measd	correlated[a]	dev/%
488.7	91.70	93.21	1.65	406.20	6.287[b]	6.407	1.89
515.5	174.9	176.9	1.13	410.30	7.605[b]	7.561	−0.57
547.5	340.6	342.7	0.63	414.25	8.851[b]	8.836	−0.17
587.4	692.9	689.8	−0.45	417.76	10.11[b]	10.12	0.03
634.4	1382	1376	−0.47	430.75	16.50[b]	16.30	−1.22
689.8	2762	2738	−0.88	459.45	42.07[b]	41.49	−1.36
711.2	3451	3487	1.04	476.06	67.66[b]	66.79	−1.29
719.2	3793	3808	0.37	492.05	101.3[b]	101.6	0.28
722.5	3966	3947	−0.47				

[a] $A = 86.5763$, $B = -10274.7$, $C = -8.74486$, $D = 2.80372 \times 10^{-18}$. [b] Ref 8.

Table 4. Vapor Pressure *p* of 1-*tert*-Butoxy-2-propanol

	p/kPa				*p*/kPa		
T/K	measd	correlated[a]	dev/%	*T*/K	measd	correlated[a]	dev/%
450.5	200.9	201.2	0.16	592.7	2414	2428	0.60
472.9	337.8	337.0	−0.25	597.5	2586	2600	0.53
510.2	689.5	691.3	0.25	598.5	2668	2637	−1.16
553.3	1380	1376	−0.27	425.15	101.3[b]	101.3	−0.03

[a] $A = 157.542$, $B = -13140.4$, $C = -19.0385$, $D = 20.4501 \times 10^{-18}$. [b] Ref 9.

Results and Discussion

Table 2a presents the measured critical point values for six of the compounds included in this study as well as estimated critical values for these compounds. These estimates were made using the boiling points measured as part of this project and the first-order atomic contribution method of Wilson and Jasperson as presented in Poling et al.[5] Test measurements on naphthalene agreed with previously published values[2−4] for the vapor pressure to within ± 2 %, to within ± 1.6 K in the critical temperature, and ± 0.08 MPa in the critical pressure. The critical temperature for 2-propene-1-ol[6] was the only other measured value found in a search of the literature. The critical temperature measured as part of this project agreed with this previous value to within ± 2 K.

Table 2b presents estimated critical point values for triacontane. The critical pressure is estimated using the boiling point determined from the vapor pressure correlation obtained as part of this project and the first-order method of Wilson and Jasperson.[5] 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. The authors feel that this was better than extrapolating to an estimated critical temperature because the normal uncertainty associated with an estimated critical temperature would translate into a large uncertainty in the extrapolated critical pressure. These values agree well with the values reported by Nikitin et al.[7]

After flowing through the apparatus, the material is collected in a receiver. Samples are taken of the material in this receiver for many of the compounds and analyzed using gas chromatography. Of these analyses, only 1-dodecanethiol shows significant decomposition, having a purity of 96 % after having flowed through the apparatus. Because the residence time before the point where the measurements are made is less than 10 % of the residence time after this point, most of this decomposition would occur after the material has exited the capillary tubing where the measurements are made. The other analyzed compounds show purities better than 99 % after having flowed through the apparatus. Significant deviations from the "normal" shape of a vapor pressure curve are a good indication of when significant decomposition is occurring.

Tables 3 through 9 present vapor pressure data on the seven 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 on these compounds. The Riedel equation[5] was used to correlate the data in this study and is given below:

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

Table 5. Vapor Pressure *p* of 2-Propene-1-ol

	p/kPa				p/kPa		
T/K	measd	correlated[a]	dev/%	T/K	measd	correlated[a]	dev/%
438.1	759.8	757.4	−0.32	370.23	101.3[b]	100.2	−1.07
465.2	1383	1394	0.81	253.15	0.1333[c]	0.1274	−4.42
498.5	2595	2638	1.65	273.35	0.6666[d]	0.6441	−3.38
531.5	4482	4496	0.31	283.65	1.333[d]	1.332	−0.07
545.4	5516	5491	−0.44	294.85	2.666[d]	2.751	3.19
546.5	5599	5576	−0.41	306.55	5.333[d]	5.504	3.21
294.15	3.040[b]	2.634	−13.34	313.45	7.999[d]	8.058	0.73
298.15	3.746[b]	3.367	−10.13	323.15	13.33[d]	13.34	0.07
303.15	4.840[b]	4.528	−6.44	337.65	26.66[d]	26.64	−0.09
308.15	6.279[b]	6.023	−4.08	353.35	53.33[d]	52.30	−1.93
313.15	8.159[b]	7.929	−2.83	369.75	101.3[d]	98.50	−2.78

[a] $A = 60.7871$, $B = -6911.46$, $C = -5.17491$, $D = 0.54729 \times 10^{-18}$. [b] Ref 10 (not used in correlation). [c] Ref 11 (not used in correlation). [d] Ref 11 (used in correlation).

Table 6. Vapor Pressure *p* of 1-Dodecanethiol

	p/kPa				p/kPa		
T/K	measd	correlated[a]	dev/%	T/K	measd	correlated[a]	dev/%
544.5	89.98	89.86	−0.13	688.6	1039	1031	−0.76
577.8	178.6	179.2	0.33	712.4	1384	1395	0.84
614.7	348.2	347.2	−0.28	729.8	1726	1723	−0.18
659.9	694.3	696.6	0.34				

[a] $A = 76.3584$, $B = -10406.0$, $C = -7.28412$, $D = 1.87142 \times 10^{-18}$.

Table 7. Vapor Pressure *p* of Thioanisole

	p/kPa				p/kPa		
T/K	measd	correlated[a]	dev/%	T/K	measd	correlated[a]	dev/%
463.7	90.87	92.05	1.30	403.878	15.74[b]	15.73	−0.05
492.1	177.3	178.5	0.64	407.306	17.73[b]	17.71	−0.11
526.3	354.1	354.2	0.02	410.756	19.92[b]	19.89	−0.12
566.1	696.4	696.8	0.06	417.664	25.01[b]	24.95	−0.22
613.6	1383	1376	−0.49	424.627	31.16[b]	31.08	−0.26
671.1	2765	2764	−0.01	431.637	38.55[b]	38.43	−0.29
691.7	3454	3470	0.45	438.698	47.36[b]	47.22	−0.30
699.9	3799	3790	−0.25	445.808	57.80[b]	57.64	−0.29
704.3	3964	3971	0.18	452.971	70.11[b]	69.93	−0.26
390.296	9.582[b]	9.613	0.33	460.186	84.53[b]	84.34	−0.22
393.680	10.88[b]	10.91	0.23	467.456	101.3[b]	101.2	−0.16
397.062	12.33[b]	12.35	0.11	474.772	120.8[b]	120.7	−0.11
400.471	13.95[b]	13.96	0.04				

[a] $A = 63.8474$, $B = -7971.93$, $C = -5.74171$, $D = 2.59201 \times 10^{-18}$. [b] Ref 12.

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 %. In the case of 2-propene-1-ol, the lowest point from Stull[11] was not used in the correlation. Using this point caused D to be less than zero, which should not occur.

Table 8. Vapor Pressure *p* of Naphthalene

	p/kPa				p/kPa		
T/K	measd	correlated[a]	dev/%	T/K	measd	correlated[a]	dev/%
502.2	128.9	129.0	0.06	410.644	10.67[c]	10.67	−0.01
552.2	337.8	340.0	0.64	417.221	13.33[c]	13.30	−0.21
646.6	1338	1353	1.15	424.055	16.67[c]	16.60	−0.38
731.8	3445	3472	0.78	429.738	19.93[c]	19.84	−0.47
741.5	3793	3823	0.81	437.222	25.02[c]	24.88	−0.57
745.9	3958	3992	0.86	437.219	25.02[c]	24.88	−0.58
441.32	28.82[b]	28.06	−2.64	444.760	31.18[c]	30.98	−0.62
462.21	49.64[b]	49.89	0.49	452.355	38.57[c]	38.32	−0.64
483.54	83.43[b]	84.69	1.52	460.002	47.38[c]	47.08	−0.62
492.37	102.0[b]	103.8	1.76	467.702	57.82[c]	57.48	−0.59
508.48	145.5[b]	147.5	1.37	475.458	70.12[c]	69.75	−0.53
526.98	211.7[b]	214.1	1.15	483.267	84.53[c]	84.15	−0.45
554.21	348.9[b]	352.0	0.90	491.130	101.3[c]	101.0	−0.37
644.26	1317[b]	1314	−0.20	499.046	120.8[c]	120.5	−0.28
672.04	1868[b]	1833	−1.92	507.020	143.3[c]	143.0	−0.17
699.82	2551[b]	2494	−2.24	515.043	169.0[c]	168.9	−0.07
727.59	3378[b]	3329	−1.48	523.123	198.5[c]	198.6	0.04
384.439	4.000[c]	4.057	1.42	531.253	232.0[c]	232.4	0.14
391.702	5.333[c]	5.381	0.90	539.434	270.0[c]	270.7	0.24
402.519	7.999[c]	8.024	0.32				

[a] $A = 52.0693$, $B = -7439.95$, $C = -4.10178$, $D = 1.37383 \times 10^{-18}$. [b] Ref 2. [c] Ref 3.

Table 9. Vapor Pressure *p* of Triacontane

	p/kPa				p/kPa		
T/K	measd	correlated[a]	dev/%	T/K	measd	correlated[a]	dev/%
713.5	82.32	81.35	−1.18	809.6	414.1	410.3	−0.92
737.8	127.8	127.8	0.02	826.3	553.6[b]	524.5	−5.26
761.2	190.2	191.5	0.68	830.1	621.9[b]	554.1	−10.90
786.0	282.4	286.0	1.28	837.6	690.2[b]	617.1	−10.58

[a] $A = 151.299$, $B = -20829.1$, $C = -16.9027$, $D = 1.92834 \times 10^{-18}$. [b] Measured vapor pressures not used in fit due to decomposition.

Table 10. Normal Boiling Points T_b Obtained from the Reported Correlations

	T_b/K	
compound	this work	previous
2-phenylethanol	491.9	492.05[a]
1-*t*-butoxy-2-propanol	425.2	425.15[b]
2-propene-1-ol	370.5	370.23[c] 369.75[d]
1-dodecanethiol	549.9	
thioanisole	467.5	467.456[e]
naphthalene	491.3	491.130[f]
triacontane	725.1	

[a] Ref 8. [b] Ref 9. [c] Ref 10. [d] Ref 11. [e] Ref 12. [f] Ref 3.

Table 10 presents the normal boiling point for each of the compounds included in this study. These values were obtained using the reported correlations given at the bottom of Tables 3 through 9. Measured boiling points reported by other researchers listed in Tables 3 through 9 are also listed. For 2-propene-1-ol, the data measured for this project only extend down to about 750 kPa. The normal boiling point reported for this compound depends strongly on which literature vapor pressures one chooses to include in the correlation. For 1-*tert*-butoxy-2-propanol, the data measured for this project extend down to about 200 kPa. The normal boiling point of Evans and Edlund[9] is in good agreement with the data measured here. For the other compounds, the data measured for this project extended to near the normal boiling point. The other normal boiling points reported in Table 10 agree well with measured values from the literature. Measured values for T_b were not found in a search of the literature for 1-dodecanethiol and triacontane.

Conclusions

Accurate vapor pressures have been measured on seven compounds of industrial significance, and reliable critical point values have been measured for six of these seven compounds. The critical point values of triacontane were not obtained using this apparatus because this compound proved too unstable. Using the measured vapor pressure data, reasonable estimates for the critical temperature and pressure of triacontane are 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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